INTERMEDIATE ORGANIC CHEMISTRY

P. B. SARKAR

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INTERMEDIATE ORGANIC CHEMISTRY

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By

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REVISED SECOND EDITION

S. C. E. R. T. West Bengal
Library
Calcutta
253, B

H. CHATTERJEE & CO. LTD.
19, SHYAMA CH. DE STREET
CALCUTTA—12

Published by
K. Sarkar, B.A.
P. 133B, Lake Terrace,
Calcutta—29.

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S.C.E.R.T., W.B. LIBRARY
Date 7.9.95
Accn. No. 9310

First published 1950
Second edition 1955

Price rupees two annas eight only

Printed by
P. B. Roy,
Prabartak Printing & Halftone Ltd.,
52/3, Bowbazar Street,
Calcutta—12.

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PREFACE TO THE SECOND EDITION

The book has been revised thoroughly and a considerable amount of new matter has been incorporated to cover the syllabuses of some universities. Typical questions have been added at the end of each chapter, some of which are from university examinations. A number of structural formulæ and equations have been included to help the students in understanding the subject. A chapter on food, identification methods for some important compounds, numerical exercises, and an index are amongst the new features of this edition. It is hoped that the book will now prove more useful to the beginners. Criticisms and suggestions for improvement will be thankfully received.

CALCUTTA
Nov. 29, 1855.

P. B. SARKAR

PREFACE TO THE FIRST EDITION

This little book, intended for the intermediate science students, is the outcome of repeated requests of some friends. Popularity of the bigger volume on the same subject has been a great inspiration, no doubt ; but having been away from the teaching profession for a pretty long time, I had to overcome much diffidence. It is for the teachers and students to judge how far these efforts have been successful. Any suggestions towards its improvement will be welcome.

CALCUTTA
March 1, 1950.

P. B. SARKAR

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CHAPTER I

Introduction.—Oils, fats, sugar, starch, gums, resins, vinegar, spirit, etc. were well known to the ancient people. They also knew how to make soap, or dye cloth with indigo. These substances, obtained from living sources such as plants or animals, were called *organic* in order to distinguish them from mineral products, *i.e.*, inorganic compounds. Considering their origin and complex nature, it was widely believed that only 'vital force' inherent in living organisms, could produce organic compounds and that they could not be synthesised in the laboratory like inorganic substances. The fact that unlike inorganic, organic compounds could not be made by directly combining the elements, supported the theory. Lavoisier (1743-94), a French chemist, first showed by analysis that *all* organic compounds contained carbon; they also contained hydrogen and oxygen, sometimes nitrogen or sulphur. Berzelius (1779-1848), a Swedish chemist, pointed out that carbon compounds obeyed the chemical laws just in the same way as those of other elements. Wöhler (1800-82), a German pupil of Berzelius, accidentally discovered in 1828 that urea (which occurs in our urine) could be made by evaporating an aqueous solution of ammonium cyanate, an inorganic salt:

$$\underset{\text{Ammonium cyanate}}{NH_4OCN} \longrightarrow \underset{\text{Urea}}{CO(NH_2)_2}.$$

Wöhler wrote to Berzelius, a staunch supporter of vital force theory, "I can make urea without requiring a kidney of an animal." Many more organic compounds were then prepared in the chemist's laboratory and it was established that there was no sharp dividing line between organic and inorganic chemistry, the same laws governed both.

Organic chemistry is thus essentially the chemistry of carbon compounds. A distinction is, however, maintained between organic and inorganic chemistry for convenience. There are now about ten lacs carbon compounds known whereas inorganic compounds number only about 75 thousand. Organic compounds resemble one another strikingly, thus all alcohols behave more or less similarly. They usually melt at low temperature and decompose at high temperature unlike inorganic compounds. Many are very complex, e.g., soluble starch has the formula $C_{1200}H_{2000}C_{1000}$. Many organic compounds unlike inorganic have the *same* molecular formula ; thus $C_{10}O_3H_{13}N$ represents 135 different compounds, $C_{10}H_{22}O$ can exist in 507 different forms. Carbon has the extraordinary capacity of combining with itself, thousands of carbon atoms may occur in a single molecule, joined each to each. Organic reactions are usually slow but inorganic reactions are almost instantaneous. Many inorganic compounds, unlike organic, dissolve in water but not in organic solvents. Cotton, paper, artificial silk, nylon, glycerine, methylated spirit, petrol, many drugs e.g., penicillin, streptomycin and chloromycetin, quinine, iodoform, etc. practically all synthetic dyes, plastics like bakelite, gums, vitamins, wool, silk, etc. are all organic compounds. Carbonates and bi-carbonates of metals, oxides of carbon, etc. are, however, included in inorganic chemistry. Some natural organic compounds contain metals, *e.g.*, hæmoglobin of blood has iron and chlorophyll of plants, magnesium.

Organic compounds are mainly derived from coal-tar, petroleum, plants and animals. But the organic chemist has synthesised an incredibly large number in the laboratory.

Purification of organic compounds.—This is essential for scientific study and medicinal use ; different methods, depending upon the nature of the compound and also of the impurities, are adopted. Some are described below.

Solvent extraction.—If a compound is more soluble in a solvent than its impurities, it can be separated therefrom by extraction with the solvent. Alcohol, ether, benzene, petroleum ether, carbon tetrachloride, etc. are commonly used as solvents. Thus alcohol can be extracted with water from its mixture with chloroform by shaking in a separating funnel (Fig. 1), chloroform being insoluble. It occupies the lower layer and is drawn off. A solid may be extracted by a hot solvent from its impurities by means of Soxhlet apparatus. Ether being sparingly soluble in water, is often used for isolating organic substances from their aqueous solutions. The compound is recovered by distilling off the solvent in each case.

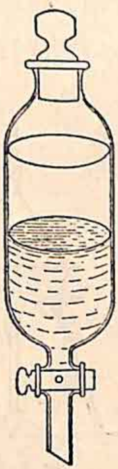
Fig. 1. Separating funnel.

Crystallisation.—Organic solids, being mostly crystalline, are generally purified by this method. It depends upon different solubilities of compounds in a solvent. The product is dissolved in the minimum quantity of a suitable solvent near about its boiling temperature, and filtered hot to prevent crystallisation during filtration (Fig. 2). Crystals separate on cooling and are removed by filtration. The process is repeated, if necessary, to obtain a compound with a sharp and constant melting

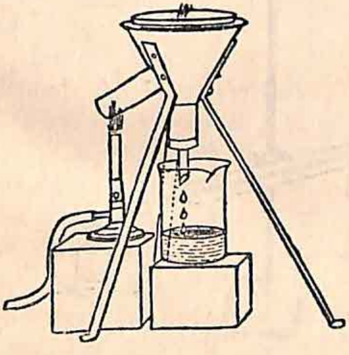
Fig. 2. Hot filtration.

point. Common solvents are water, alcohol, benzene, ether, acetic acid, acetone, etc.

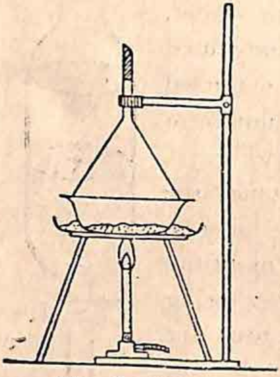

Fig. 3. Sublimation.

Sublimation.—Some organic solids like camphor or naphthalene, sublime, *i.e.,* turn directly into vapour on heating without first becoming a liquid. They can easily be separated from others which do not sublime, by heating on a sand-bath in a basin covered with a funnel with its stem closed with cotton wool. The deposit on the inner wall of the funnel is the pure product.

Distillation.—This is the most common way of purifying an organic liquid. As a rule, different compounds have different boiling points (b.p.). When the difference in boiling points of two liquids is appreciable, the low-boiling one

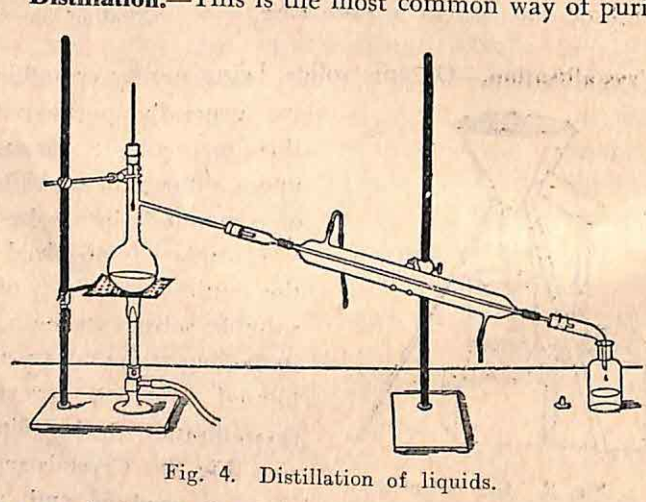

Fig. 4. Distillation of liquids.

comes out first on distilling and is condensed. A second distillation may be necessary to obtain it in the pure form. Benzene (b.p. 80.4°) can thus be separated from nitrobenzene (b.p. 209°) which comes over when practically all the benzene has gone off. This is called *fractional distillation*. An air condenser is used for liquids boiling above 130°. Bumping is avoided by adding a few pieces of unglazed porcelain.

If, however, the boiling points lie close together, a fractionating column is vertically inserted between the distilling flask and the condenser before distillation. By this device, the more volatile liquid may be separated from the mixture. Alcohol (b.p. 78.5°) is thus separated from water (b.p. 100°). On heating, both water and alcohol vaporise but the vapour consists of a larger proportion of alcohol. As it goes up the column, water vapour condenses *more rapidly* so that mostly alcohol comes over. The process is repeated to get a pure product. If the liquid decomposes at or below its b.p. at atmospheric pressure, it may be purified by distillation under reduced pressure. This is called *vacuum distillation*. A liquid boils at a lower temperature if the pressure is lowered.

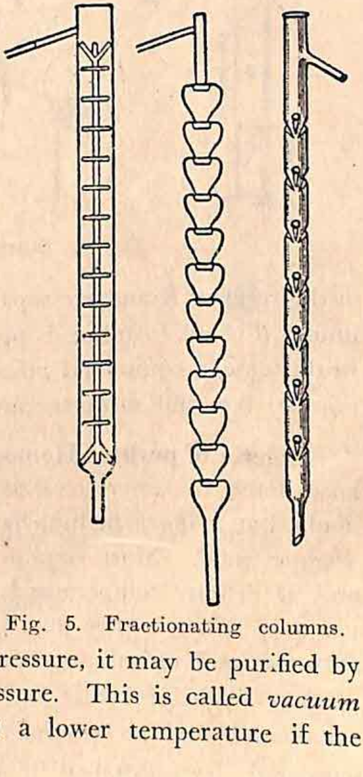
Fig. 5. Fractionating columns.

Steam-distillation.—If a compound is volatile in steam but insoluble in water, it can be separated from non-volatile impurities by steam distillation. Rose oil is extracted from the flowers likewise. The substance with some water is heated in the round-bottomed flask F and steam from the can B is passed through it. Water and the substance collect in the receiver R and are separated by means of a separating funnel (Fig. 6). Aniline is purified by distillation in steam. In this case, a compound boils at a much lower temperature than its b.p. and so decomposition is avoided.

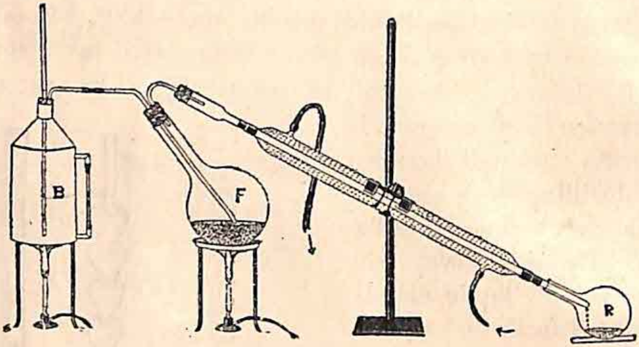

Fig. 6. Steam distillation.

Criteria of purity.—Homogeneous and crystalline appearance under the microscope is generally a sign of purity, no doubt, but a *sharp* melting point is the best criterion for an organic solid. Most organic substances melt below 300° and at definite temperatures. Impurities, as a rule, lower the m.p. That is why m.p. gradually rises as impurities are removed, and ultimately, becomes constant. Determination of m.p. is helpful also in the identification of organic compounds and is generally done by taking the finely powdered, dry substance in a capillary tube closed at one end, and gradually heating it in a sulphuric acid bath, attached to the end of a thermometer (Fig. 7). Glycerol, liquid paraffin or castor oil may also be used in place of sulphuric acid.

An organic liquid is considered pure if it has a *sharp* boiling point which remains constant provided the atmospheric pressure is constant. The b.p. is determined by slowly heating the dried liquid in a distilling flask fitted with a thermometer (which must be above the liquid) and a condenser (Fig. 4). A few pieces of pumice stone or unglazed porcelain may be added to the liquid to avoid bumping. If the liquid is pure, it comes over at a constant and definite temperature; a constant-boiling mixture like rectified spirit (having about 96% of alcohol and 4% of water), however, distils unchanged.

Moisture adheres to most organic compounds and has to be removed before analysis. Depending upon the nature of the compound, various methods are employed. Solids are generally dried in steam- or air-oven as well as over calcium chloride or conc. H_2SO_4 in desiccators preferably under vacuum; liquids are dehydrated by shaking with fused calcium chloride, quicklime, caustic soda, etc. Gases are usually dried by passing through conc. H_2SO_4 in gas washers or soda-lime in towers.

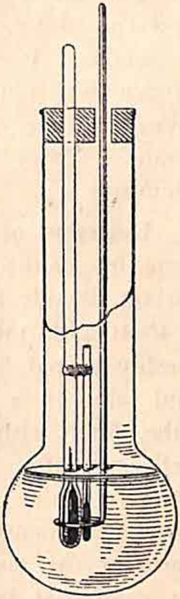

Fig. 7. Determination of melting point.

Questions

1. Discuss briefly some of the features that distinguish organic compounds from inorganic ones. I.Sc. 1955, Patna Uni.

2. Explain with examples any three of the following for purifying an organic substance: fractional distillation, steam distillation, distillation, vacuum distillation, crystallisation and extraction with a solvent. How do you ascertain that the sample obtained is pure? I.Sc. 1952, E. Punjab Uni.

3. What are the different methods by which organic compounds are purified?

CHAPTER II

Qualitative analysis.—To ascertain the molecular formula of a compound, it is first necessary to detect the elements it contains. As already mentioned, usually carbon, hydrogen, oxygen, nitrogen, halogens, sulphur, phosphorus and metals occur in these compounds, the first four being the most common; they are, in fact, the "Big Four" of organic chemistry.

Detection of carbon and hydrogen.—This is invariably done by oxidising the compound with cupric oxide to carbon dioxide and water. A little of the *dried* substance is thoroughly mixed with about twenty times its weight of freshly-ignited, fine copper oxide and taken in a hard glass test-tube, fitted with a cork and a delivery tube. It is heated strongly, the water vapour formed condenses in the cooler parts of the test-tube and may be confirmed by adding anhydrous copper sulphate which turns blue. The end of the delivery tube leads to a test-tube containing lime-water which turns turbid with carbon dioxide. If the compound be a volatile liquid or a gas, the vapour of the liquid or the gas itself is passed through a red-hot glass tube containing coarse, ignited copper oxide. The outcoming gas is tested for water and carbon dioxide as usual.

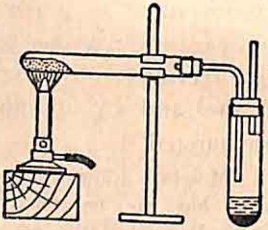

Fig. 8. Detection of carbon and hydrogen.

Detection of nitrogen.—A little metallic sodium and a pinch of the compound are taken in an ignition tube and heated to redness until action ceases. A black mass is thus obtained. The hot tube is plunged into water in a porcelain mortar and the crumbled pieces powdered. The solution is filtered. To the filtrate taken in a test-tube, about 1 c.c. of freshly prepared ferrous sulphate solution is added. The mixture is boiled for a minute. The solution is cooled, 1-2 drops of ferric chloride solution added, and made acid with hydrochloric acid. A blue colour or precipitate of Prussian blue indicates the presence of nitrogen in the original substance. This is *Lassaigne's test*. During fusion, nitrogen and carbon of the compound combine with sodium forming sodium cyanide, NaCN; this, on boiling with ferrous hydroxide (resulting from ferrous sulphate and caustic soda), gives sodium ferrocyanide. With ferric chloride and acidified solution of ferrocyanide, Prussian blue is obtained:

$$6NaCN + Fe(OH)_2 = \underset{\text{Sodium ferrocyanide}}{Na_4Fe(CN)_6} + 2NaOH$$

$$4FeCl_3 + 3Na_4Fe(CN)_6 = \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl.$$

Detection of halogens.—The compound is fused with sodium as above, sodium halides thus result, if halogens are present. The filtrate is boiled with excess of nitric acid to expel sulphuretted hydrogen, H_2S, and hydrocyanic acid, HCN, if sulphur and nitrogen also occur. On adding silver nitrate solution, a curdy white or yellow precipitate (ppt.) indicates halogen. The silver halide is identified in the usual way with ammonia. A halogen in an organic compound cannot be directly detected with silver nitrate solution, as it does not split up into charged atoms (or ions) in solution like inorganic halides.

Detection of sulphur.—The substance is fused with sodium as in the case of nitrogen, sodium sulphide, Na_2S, is thus formed. A violet colour, the extract gives with a drop of freshly prepared solution of sodium nitro-prusside, indicates sulphur. A black ppt. of lead sulphide is also formed when lead acetate is added to the original filtrate acidified with acetic acid.

Detection of phosphorus.—On heating the compound with fusion mixture (sodium carbonate and potassium nitrate), sodium phosphate is obtained by oxidation. The hot water extract of the fused mass is acidified with nitric acid and ammonium molybdate solution added. A heavy, yellow ppt. indicates phosphorus.

Detection of oxygen.—There is no simple method for this; some dry compounds, on heating strongly, liberate water, showing indirectly the presence of oxygen. Existence of groups like $>CO$, $-OH$, $-NO_2$, $-COOH$, $-CHO$, etc. in a compound, shown otherwise, indicates its presence. If the percentage values of other elements do not make 100, the difference is due to oxygen.

Detection of metals.—On ignition of the compound, an oxide or carbonate of the metal is left as residue; it is then tested in the usual way as in inorganic chemistry.

Quantitative analysis.—To determine the composition and structure of a compound, it is necessary to know the elements which build up the compound and the proportion in which they occur. Estimation of the constituent elements is an important operation.

Estimation of carbon and hydrogen.—All organic compounds are *completely* broken up into carbon dioxide and water on strongly heating with cupric oxide. These are separately absorbed by suitable arrangements and weighed. The weight of the substance taken for analysis being known, the amounts of carbon and hydrogen (which are invariably estimated together) in the compound can be easily calculated. The method, known as combustion, is mainly due to Liebig.

0·1-0·2 g. of the powdered and dried substance is taken in a porcelain boat (c) which is placed in the combustion tube, made of hard glass, about $\frac{2}{3}$ of which is filled with coarse copper oxide (p-p′ in Fig. 9). It is connected with a rubber tube at one end to a weighed U-tube filled with granulated calcium chloride and then to a weighed potash bulb containing 50% caustic potash solution. The free end of the potash bulb carries a small guard tube, half-filled with soda-lime. A spiral roll of copper gauze (B), coated with copper oxide by heating in air, is placed behind the boat to prevent backward diffusion of combustion products.

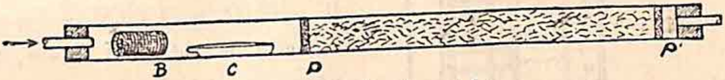

Fig. 9. Combustion tube.

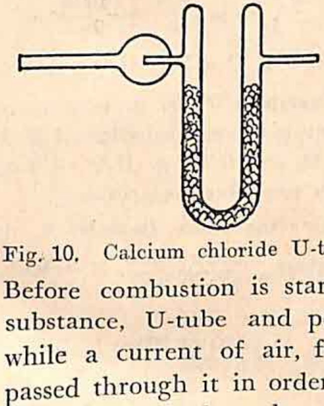

Fig. 10. Calcium chloride U-tube.

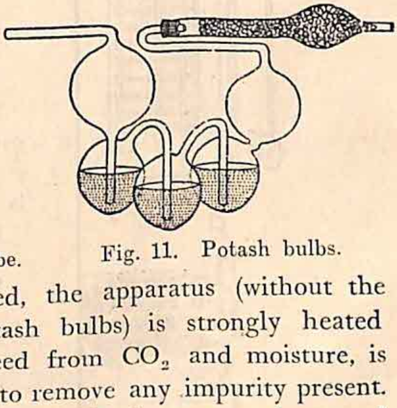

Fig. 11. Potash bulbs.

Before combustion is started, the apparatus (without the substance, U-tube and potash bulbs) is strongly heated while a current of air, freed from CO_2 and moisture, is passed through it in order to remove any impurity present. Air is passed through conc. H_2SO_4 in gas washers and through soda-lime in U-tubes to remove moisture and CO_2 from it. The combustion tube is then gradually heated from both ends, proceeding towards the boat while purified air or oxygen is passed slowly through it. The combustion is complete when nothing is left on the boat. It usually takes about two hours. The apparatus is cooled; the U-tube and the potash bulbs are stoppered and then weighed. *All connections must be air-tight.*

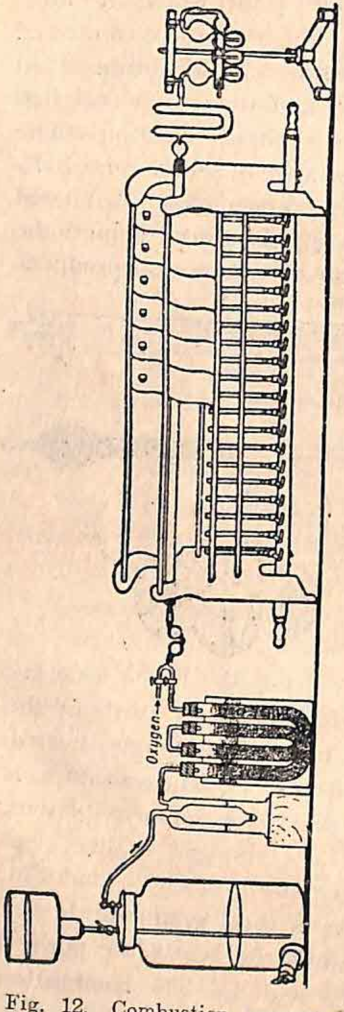

Fig. 12. Combustion apparatus for estimation of carbon and hydrogen.

Let w = weight of substance taken,

w_1 = increase in weight of the potash bulb,

w_2 = increase in weight of the U-tube.

∴ weight of $CO_2 = w_1$ g.

whence % of carbon =

$$\frac{12\times w_1}{44}\times\frac{100}{w}=\frac{300w_1}{11w}$$

$(C = 12,\ O_2 = 32\ ;\ CO_2 = 44)$.

Similarly, weight of $H_2O = w_2$ g.

whence % of hydrogen =

$$\frac{2\times w_2}{18}\times\frac{100}{w}=\frac{100w_2}{9w}\ .$$

$(H_2 = 2,\ O = 16\ ;\ H_2O = 18)$.

Example: 0·3560 g. of a compound gave on combustion 1·2220 g. CO_2 and 0·200 g. H_2O. What is its percentage composition?

Using the above formula, % of carbon $=\dfrac{300\times1{\cdot}2220}{11\times0{\cdot}3560}$ or 93·62.

and % of hydrogen

$$=\frac{100\times0{\cdot}200}{9\times0{\cdot}3560}\ \text{or}\ 6{\cdot}24.$$

The compound, therefore, contains no other element.

If the substance has nitrogen, a bright roll of metallic copper gauze is placed in the combustion tube, beyond copper oxide, towards the U-tube to reduce the oxides of nitrogen formed to nitrogen. In case it contains halogens or sulphur, coarse copper oxide is replaced by fused lead chromate, halide or sulphate of lead is thus formed so that free halogens or sulphur dioxide may not be absorbed by the potash bulbs to vitiate the result.

Determination of nitrogen.—Organic nitrogenous compounds split up into carbon dioxide, water, nitrogen and to some extent, its oxides on heating strongly with copper oxide. These are passed over a heated copper gauze to reduce the oxides of nitrogen to nitrogen, and then collected over caustic potash which absorbs CO_2. The volume of nitrogen thus collected is measured, and knowing the weight of the compound taken, the percentage of nitrogen in it is readily calculated.

$$\begin{array}{r} \text{Substance} + CuO \xrightarrow{\text{heat}} CO_2 + H_2O + N_2 + \text{Oxides of } N_2 \\ \big\downarrow \text{Cu gauze} \\ N_2 + H_2O \xleftarrow{\text{KOH}} CO_2 + H_2O + N_2 \end{array}$$

The portion AB of the combustion tube (Fig. 13) is packed with coarse copper oxide, BC is a mixture of the weighed amount of the compound with fine copper oxide, CD is also packed with coarse copper oxide and E is a bright spiral of copper gauze. The end is connected with a rubber tube to a finely graduated nitrometer, N, containing 40% KOH solution.

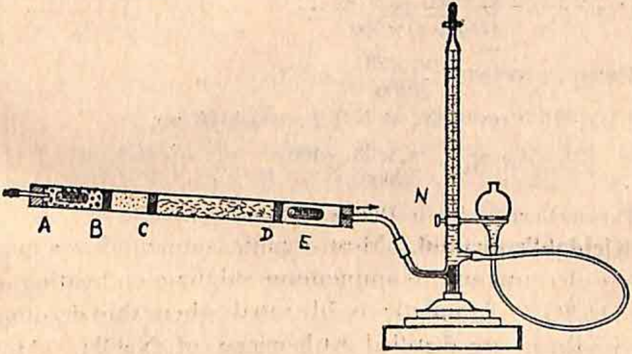

Fig. 13. Estimation of nitrogen by Dumas' method.

A hard glass tube, closed at one end, containing sodium bicarbonate, is connected through a gas washer containing conc. H_2SO_4, to the other end of the combustion tube. The bicarbonate tube generates pure CO_2 on heating; a slow stream of the gas is continuously passed through the combustion tube. It expels any air inside the combustion tube (which is disconnected from the nitrometer). The combustion tube is then heated gradually till no more nitrogen is evolved. The products are swept from the combustion tube. After cooling, the gas is measured making the level inside and out the same, the temperature and barometric pressure are also noted.

Let v_1 = volume of N_2 collected,
$t°C$ = temperature of the room,
P = barometric pressure,
p = aqueous tension at $t°C$,
v_2 = volume the gas would occupy at N.T.P.
w = weight of the substance taken.

Then, $v_2 = \dfrac{v_1 \times (P-p) \times 273}{(273+t) \times 760}$.

Thus w g contains $\dfrac{v_2 \times 28}{22400}$ g of N_2,

($\because$ 22·4 litres of N_2 at N.T.P. weigh 28 g.)

$$\therefore \ \% \text{ of } N_2 = \frac{v_2 \times 28}{22400} \times \frac{100}{w} = \frac{v_2}{8w}.$$

This method is due to Dumas, a French chemist.

Kjeldahl's method.—Most organic compounds are quantitatively decomposed to ammonium sulphate on heating with conc. H_2SO_4. Ammonia is liberated when the decomposition products are distilled with excess of NaOH. This is absorbed by a known volume of standard acid and the amount of ammonia determined by back titration with standard alkali

0·5 - 5 g. of the substance, depending upon the amount of nitrogen present, is heated with about 20 c.c. of conc.

H_2SO_4 in a Kjeldahl's flask in a fume chamber until the liquid becomes almost colourless. About 10 g. of K_2SO_4 is added to raise the boiling point of H_2SO_4 ; this helps decomposition. A small crystal of copper sulphate which acts as a catalyst is also added. The cooled liquid is diluted with water, taken to a flask and distilled immediately after adding about 80 c.c. of a 40% NaOH solution. The flask is connected to a condenser the end of which dips into a known volume of N/10 H_2SO_4 containing a few drops of methyl orange indicator. The acid in the conical flask is titrated with N/10 NaOH when no more ammonia comes over.

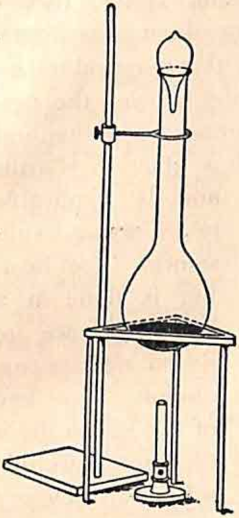

Fig. 14. Kjeldahl's flask.

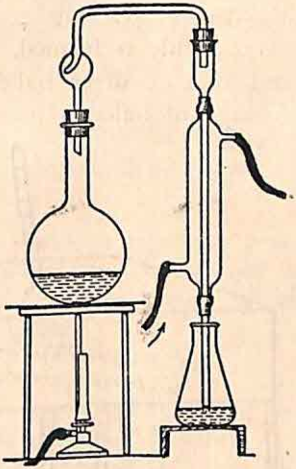

Fig. 15. Kjeldahl's estimation of nitrogen.

Calculation: If v c.c. of normal acid is thus consumed, v/1000 equivalents of ammonia have been obtained, which means $\frac{v \times 14}{1000}$ g. of nitrogen. If w g. of the substance was taken,

$$\% \text{ of } N_2 = \frac{v \times 14}{1000} \times \frac{100}{w} = \frac{1{\cdot}4v}{w}.$$

Estimation of halogens.—When an organic compound (0·2 - 0·3 g.) containing halogen is heated under pressure in a sealed, Jena glass tube with fuming HNO_3 (about 3 c.c.) and silver nitrate to about 250° for about four hours, silver halide is formed. The weight of the material taken and that of silver halide obtained being known, the percentage of halogen present is readily found. The method is due to Carius and is applicable to *all* organic substances. The heating is done in a bomb furnace to guard against explosion. One end of the glass tube is then carefully softened by a flame when the gas inside it mostly escapes. The contents are taken out, diluted with water, boiled and weighed after filtration and drying.

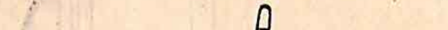

Fig. 16. Carius' estimation of halogens. Bomb furnace

Calculation: If w_1 g. of the compound gives w_2 g. of silver chloride (say), it contains

$$\frac{w_2 \times 35{\cdot}5}{108+35{\cdot}5} \text{ g. of chlorine.}$$

$$\therefore \ \% \text{ of chlorine} = \frac{35{\cdot}5 \times w_2}{143{\cdot}5} \times \frac{100}{w_1} .$$

Estimation of sulphur and phosphorus.— This is done as in the case of halogens but without adding silver nitrate. Sulphur in organic compounds is oxidised to sulphuric acid by nitric acid. The sulphuric acid is precipitated with barium chloride solution as barium sulphate which is weighed after filtration, washing and drying. Phosphorus is thus oxidised to phosphoric acid quantitatively, which is precipitated as magnesium pyrophosphate and weighed.

Estimation of oxygen.— No simple method exists for this, the usual procedure is to find the percentage of oxygen by difference when the amounts of all other elements present in an organic compound are precisely known.

If necessary, the oxygen in such a compound may be estimated by heating it strongly in a current of hydrogen and passing the vapour over heated nickel. Water is thus formed from oxygen, and is absorbed by calcium chloride as usual.

Questions

1. How would you detect the presence of nitrogen, sulphur and chlorine in an organic compound? Give experimental details.

I.Sc. 1955, Patna Uni.

2. Describe the Carius' method for estimating halogens.

3. Calculate the percentage of nitrogen from the following data : 0·5 g of substance was decomposed and distilled with NaOH and the ammonia collected in 50 c.c. normal H_2SO_4. The excess acid required 33·6 c.c. of normal NaOH for neutralisation.

4. How would you estimate the percentage of nitrogen in an organic compound?

5. Calculate the weight of CO_2 and H_2O that can be obtained by combustion of 0·1 g. of an organic substance having the molecular formula C_9H_9ON. I.Sc. 1952, Poona University.

CHAPTER III

Empirical formula of an organic compound.— Elementary quantitative analysis gives only the percentage composition of a compound. The ratio, obtained by dividing the percentage weight of each element by its atomic weight, is expressed in whole numbers by dividing, if necessary, each quotient by the lowest one, or by a simple fraction of it. The simplest formula, corresponding to the percentage composition of the compound, thus obtained is known as its *empirical formula*. It represents the ratio of the atoms in the molecule. Illustrations will make it clear.

Example I. A compound, on analysis, gave C = 83·7% and H = 16·28%. What is its empirical formula?

By dividing the percentage composition by respective atomic weights (at. wt.), we have

$$H = \frac{16{\cdot}28}{1{\cdot}008} = 16 \text{ approximately}$$

$$C = \frac{83{\cdot}7}{12{\cdot}0} = 7 \quad \text{,,}$$

Hence the empirical formula is C_7H_{16}, the molecular formula may be C_7H_{16} or a multiple of it, $(C_7H_{16})_n$, where n is a whole number. If we know the molecular weight (mol. wt.), we can find n.

Example II. A compound has C = 48·8% and H = 3·1%. Find its empirical formula.

Since C and H together make 51·9% only, the rest 48·1% is O.

$$\text{Hence } C = \frac{48{\cdot}8}{12{\cdot}0} = 4 \text{ approximately}$$

$$H = \frac{3{\cdot}1}{1{\cdot}008} = 3 \quad \text{,,}$$

$$O = \frac{48{\cdot}1}{16{\cdot}0} = 3 \quad \text{,,}$$

∴ The empirical formula is $C_4H_3O_3$.

Example III. An organic compound has C = 43·98%, H = 2·09%, Cl = 37·18%. Calculate its empirical formula.

Here O (by difference) = 16·75%.

The relative number of atoms are :

$$C = \frac{43{\cdot}98}{12{\cdot}0} = 3{\cdot}66$$

$$H = \frac{2{\cdot}09}{1{\cdot}008} = 2{\cdot}07$$

$$Cl = \frac{37{\cdot}18}{35{\cdot}5} = 1{\cdot}05$$

$$O = \frac{16{\cdot}75}{16{\cdot}0} = 1{\cdot}04$$

Dividing these by the smallest one *viz.* 1·04, we have C_3H_2OCl to the nearest accuracy as the empirical formula.

Molecular formula.—While an empirical formula gives the *relative* number of atoms of different elements in a compound, a molecular formula expresses the *exact* number of these atoms in the molecule. Molecular formula can be arrived at only when we know the mol. wt. of the compound. The empirical formula of alcohol is C_2H_6O, its molecular formula is $(C_2H_6O)n$; since its molecular weight is 46, n = 1 *i.e.*, its molecular formula is the same as its empirical formula. Benzene has a mol. wt. of 78 and its empirical formula is C_1H_1, so that its molecular formula is C_6H_6. Determination of mol. wt. of organic compounds is, therefore, important.

Determination of mol. wt.—Since from Avogadro's hypothesis the relative density of a gas or vapour is half its mol. wt. (*i.e.*, mol. wt. = 2 × vapour density), the mol. wt. of *volatile* organic compounds can be calculated if we can somehow determine their vapour density. We have to find the volume a given weight of the substance would occupy in gaseous form at a known temperature and pressure. This can be done by three different methods.

(1) Victor Meyer's method.—The apparatus consists of a long glass bulb with a long, narrow stem and a capillary, bent tube at the side. This is housed in a copper jacket, containing a liquid with a b.p. at least 25°C higher than that of the substance under examination. The side-tube leads to a graduated tube filled with water and inverted over a trough of water. The liquid in the copper vessel is boiled and a definite weight of the substance in a small, closed bottle or glass tube sealed at both ends is quickly introduced into the bulb (when no more air issues out from the apparatus) and closed immediately with a rubber cork. The substance rapidly vaporises and an equivalent amount of displaced air collects in the graduated tube. When no more bubbles issue out, the volume of the air is noted and also the temperature and pressure.

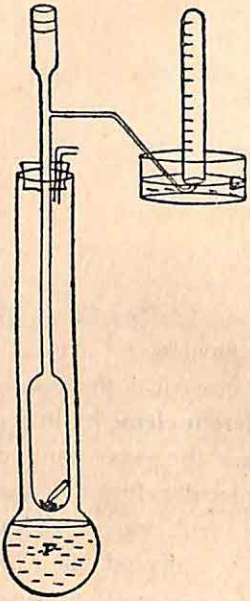

Fig. 16. Victor Meyer's apparatus.

Calculation: If V_1 c.c. of air was displaced at t_1 °C and P_1 cm, (p cm being the aqueous tension at t_1 °C), its volume V, at N.T.P. would be $\frac{(P_1-p)\times V_1}{(273+t_1)}\times\frac{273}{76}$ c.c.

$\therefore$ Vapour density $= \frac{w}{V\times 0{\cdot}00009}$, w g. being the wt. of the substance and 0·00009 the density of H_2.

Hence the mol. wt. $= \frac{2\times w}{V\times 0{\cdot}00009}$

Example: 0·1680 g. of a substance expelled 49·4 c.c of air at

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20°C and 740 mm. What is its mol. wt.? Aqueous tension at 20°C is 18 mm.

$$\text{Volume of vapour at N.T.P.} = \frac{49{\cdot}4\times(740-18)\times273}{293\times760}\text{ c.c.}$$

$$\therefore\ \text{Vapour density} = \frac{0{\cdot}1680\times293\times760}{49{\cdot}4\times722\times273\times0{\cdot}00009}$$

$$\therefore\ \text{Mol. wt.} = \frac{2\times0{\cdot}1680\times293\times760}{49{\cdot}4\times722\times273\times0{\cdot}00009} = 85{\cdot}39.$$

This method cannot be applied to non-volatile substances or to compounds that decompose on vaporisation. Hofmann's method, in which the compound is vaporised under reduced pressure over mercury, may be employed for the latter, and cryoscopic or ebullioscopic method for the former kind of organic compounds.

(2) Cryoscopic method.—Gram molecular weights of different substances, dissolved in the same quantity of a solvent, lower the freezing point of the solvent to the *same* extent, provided the solution is dilute. This lowering of freezing point is proportional to the concentration of the solute. Thus if w g. of a substance be dissolved in W g. of solvent of freezing point $t_1°$, and the freezing point of the solution is found to be $t_2°$, the mol. wt. of the substance, $M = \frac{C\times w\times100}{(t_1-t_2)\times W}$, where C is a constant which is different for different solvents. For water, C is 18·8, for phenol it is 72, for acetic acid, 39, for benzene, 50, and so on.

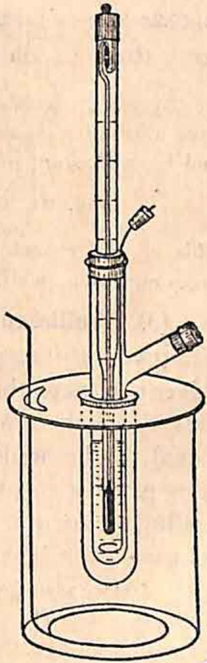

Fig. 17. Freezing point Apparatus (Beckmann).

Beckmann's apparatus is used for this purpose, and consists of a large glass tube with a side-tube. A Beckmann thermometer which covers a range of only 5°–6° graduated in 0·01°, and records

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not the actual but the difference of temperature, is inserted into the tube. This tube is placed in a wider glass tube which is placed in a cold bath having a temperature at least 5° below the m.p. of the solvent. The bath is stirred with a stirrer by hand while the innermost tube is stirred with an electric stirrer. The operation is simple; a known weight of a pure solvent is first introduced into the Beckmann tube and its freezing point determined accurately. Then 0·2 to 1·5 g. of the substance is introduced through the side-tube, the solvent liquefied and freezing point of the solution found. The difference between the freezing points $(t_1 - t_2)$ is thus known; mol. wt. of the substance can be calculated from the formula given above.

Example: 2·093 g. of a substance dissolved in 100 g. of benzene gave a solution freezing at 4·440°; pure benzene freezes at 5·440° and has a constant of 50. Calculate the mol. wt. of the substance.

$$\text{Mol. wt.} = \frac{50 \times 2{\cdot}093 \times 100}{(5{\cdot}440 - 4{\cdot}440) \times 100} = 104{\cdot}6.$$

This method cannot be applied to electrolytes e.g., organic acids, bases and salts, which ionise in solution.

(3) Ebullioscopic method.—Gram molecular weights of different substances, dissolved in the same quantity of a solvent, elevate the boiling point of the solvent to the *same* extent. If the solution is dilute, the rise in b. p. is proportional to the molecular concentration of the solute. Thus if w g. of a substance be dissolved in W g. of a solvent of boiling point t_1°, and the boiling point of the resulting solution is t_2°, the molecular weight of the substance, $M = \frac{100 \times c \times w}{(t_2 - t_1) \times W}$ where c is a constant characteristic of the solvent. For water, it is 5·2, for benzene, 26·7, for acetic acid 25·3 and so on.

Beckmann's apparatus is employed for this purpose. A definite weight of pure solvent is boiled in the tube fitted with a condenser and a Beckmann thermometer. The tube is heated by the outer jacket containing a boiling liquid and carrying a condenser. The boiling point is noted and a weighed amount of the substance is introduced through the side-tube. The b.p. is again noted. The difference between the two readings gives the elevation in boiling point.

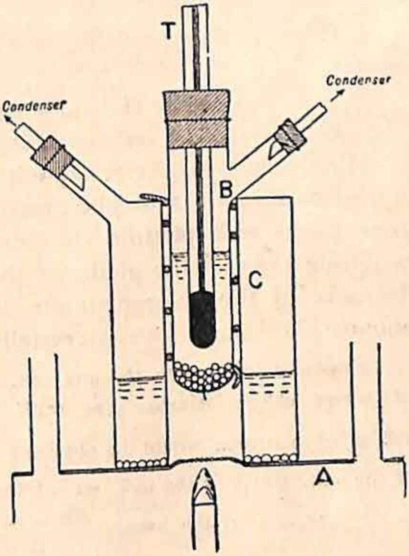


Fig. 18. Beckmann's Boiling-point Apparatus.

Example: 0·7269 g. of a substance dissolved in 32·08 g. of acetone (b.p. 56·30°) boiled at 56·55°. Find the mol. wt. of the substance, the constant for acetone being 16·74.

$$\text{Mol. wt.} = \frac{100 \times 16{\cdot}74 \times 0{\cdot}7269}{(56{\cdot}55 - 56{\cdot}30) \times 32{\cdot}08} = 148{\cdot}4.$$

Molecular weights of electrolytes cannot be found by this method.

Mol. wts. of organic acids and bases.—The equivalent weight of an organic acid can be determined, much in the same way as that of inorganic acids, by titrating a known weight (0·2-·05 g.) of it dissolved in aqueous alcohol with decinormal caustic soda solution, using phenolphthalein as indicator. The mol. wt. of the acid can be found by multiplying the equivalent weight with its basicity.

The equivalent weight of many organic acids can also be found by igniting a weighed quantity of the silver salt (which is usually sparingly soluble in water) and weighing the metallic silver thus obtained.

Example: 0·7692 g. of a monobasic silver salt gave on ignition 0·3625 g. of metallic silver. Calculate the mol. wt. of the acid.

108 g. of silver would be obtained from $\frac{0 \cdot 7692}{0 \cdot 3625} \times 108$ g. i.e. 229·18 g. of salt.

$\therefore$ the mol. wt. of the acid $= 229 \cdot 18 - 108 + 1 = 122 \cdot 18$.

(one atom of silver replaces one atom of hydrogen from the acid).

Equivalent weight of organic bases is commonly determined by igniting a weighed quantity of chloroplatinate the base forms with platinic chloride in presence of HCl and weighing the metallic platinum thus obtained. The general formula of the chloroplatinate is $B_2H_2PtCl_6$ (B being a monoacidic base). This is crystalline and so, easy to purify.

Example: Calculate the mol. wt. of a monoacid base, 0·596 g. of whose chloroplatinate gave 0·195 g. of platinum on ignition. 195 g. of platinum would be obtained from $\frac{0 \cdot 596}{0 \cdot 195} \times 195$ i.e., 596 g. of the salt, which is the mol. wt. of the salt.

$\therefore$ mol. wt. of the base $= \frac{596 - 410 \cdot 2}{2} = 92 \cdot 9$. ($H_2PtCl_6 = 410 \cdot 2$).

Questions

1. 0·300 g of an organic compound gave 0·574 g of CO_2 and 0·351 g of H_2O. Its vapour density is 23. What is its molecular formula?
I.Sc. 1951, Nagpur University.

2. What is meant by the empirical and the molecular formula of a compound? How are the two related? Give examples.

3. An organic compound gave 43·98% C, 37·18% Cl and 2·09% H on analysis. Calculate its empirical formula. If it is a mono-basic acid, what is its molecular formula?

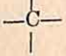
4. 0·6 g of a solid was dissolved in 10 c.c. of acetone, the b.p. was elevated by 1·67°C. Calculate its mol. wt. (K for acetone is 16·7).

5. How is the mol. wt. of a substance determined in solution by noting the lowering of the freezing point of the solvent?

6. An organic monobasic acid having only C, H and O, gave on analysis 70·58% C and 5·88% H. Its silver salt gave on ignition 44·44% Ag. What is its molecular formula?

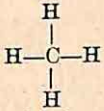
CHAPTER IV

Classification of organic compounds.—Carbon has the unique capacity of combining with oxygen and hydrogen in various ways to form an incredibly large number of compounds. Carbon is tetravalent, *i.e.*, it combines with four mono-valent elements or groups (or radicals). This is graphically represented as follows. Each stroke (or single bond) between two atoms indicates the combination of one valency of each.



$$\begin{array}{ccc} & | & \\ - & C & - \\ & | & \end{array}$$

Tetravalent carbon



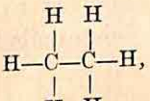
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

Methane

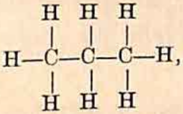
Carbon exhibits this tetravalency in practically all compounds in a striking manner. Much more striking is the fact that it can combine with itself almost indefinitely by one or more valency bonds. Kekulé, a young German lecturer, based his theory of organic molecular structure on these two postulates in 1858. Two or three strokes between two elements represent the mutual engagement of four or six valencies in two or three pairs. These are known as *double* and *triple* bonds respectively.

$\equiv C-C\equiv \qquad =C=C= \qquad -C\equiv C-$

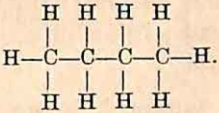
Thus ethane, propane and butane are respectively



$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C- & H, \\ & | & | & \\ & H & H & \end{array}$$

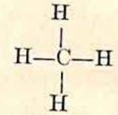
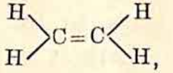


$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C- & H, \\ & | & | & | & \\ & H & H & H & \end{array}$$



$$\begin{array}{cccccc} & H & H & H & H & \\ & | & | & | & | & \\ H- & C- & C- & C- & C- & H. \\ & | & | & | & | & \\ & H & H & H & H & \end{array}$$

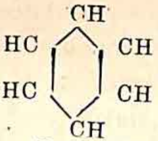
This chain of carbon atoms may have any length; for example, a compound with 94 atoms of carbon and 190 hydrogen atoms has been prepared in the laboratory.

A compound with a double or a triple bond is called *unsaturated*; in case it has only single linkages, it is termed *saturated*. Thus methane,  $H-\overset{H}{\underset{H}{C}}-H$ is a saturated compound but ethylene,  is unsaturated. Compounds of carbon and hydrogen are known as *hydrocarbons*.

The carbon chain may be open, or closed in the form of a ring ; for convenience we sub-divide organic compounds into two main groups, *viz.*, (*i*) open-chain or *aliphatic* compounds and (*ii*) closed-chain or *aromatic* compounds. The Greek word *aleiphar* means fat ; since all fats have open-chain structure, other open-chain compounds are called *aliphatic*. These may be regarded as derivatives of methane, CH_4. Aromatic compounds were so called originally because of the *aroma* or smell many of them possessed. They were later on found to have ring structure. They may be looked upon as derivatives of benzene.

$H_3C-CH_2-CH_2-CH_2-CH_2-CH_3$ and

Hexane (aliphatic)



Benzene (aromatic)

These two types cover practically the vast field of organic chemistry but we shall, in the beginning, cover only a small portion of it. We take up aliphatic compounds first as usual.

Saturated hydrocarbons or paraffins.—The simplest of organic compounds are the hydrocarbons—they are important as mother substances of other aliphatic compounds. The saturated hydrocarbons or *alkanes* are more commonly known as **paraffins** (*parum* little, *affinis* affinity) because they are quite unreactive. Ordinary chemical reagents have little effect on them. Methane is the simplest hydrocarbon; we, therefore, start with this.

Methane, CH_4, is a gas that arises from decaying plants in pools and marshes and so called *marsh-gas*. It forms about 85% of the *natural gas* coming from oil-wells in petroleum districts. The 'eternal fires of Baku' were due to burning of natural gas in the oil fields. The gas also occurs in coal-mines and was once the cause of frequent explosions. Miners call it *fire-damp* (*damp* gas). Coal-gas contains about 40% of methane by volume.

Preparation.—(*i*) In the laboratory, methane is usually prepared by heating fused sodium acetate with three times its weight of soda-lime (quick-lime slaked with conc. NaOH solution and dried) in a hard glass test-tube. The gas is collected over water. It is not, however, quite pure.

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH = \underset{\text{Methane}}{CH_4} + Na_2CO_3.$$

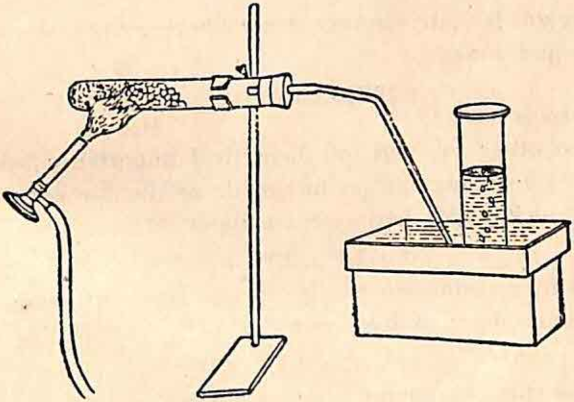


Fig. 19. Preparation of methane.

(*ii*) Pure methane may be obtained by adding methyl iodide from a separating funnel to zinc-copper couple (granulated zinc coated with a thin layer of copper by treating with a solution of copper sulphate) in presence of alcohol or water, taken in a flask. Nascent hydrogen, liberated from alcohol or water by the couple, reacts with methyl iodide to yield methane at room temperature.

$$\underset{\text{Methyl iodide}}{CH_3I} + 2H = \underset{\text{Methane}}{CH_4} + HI.$$

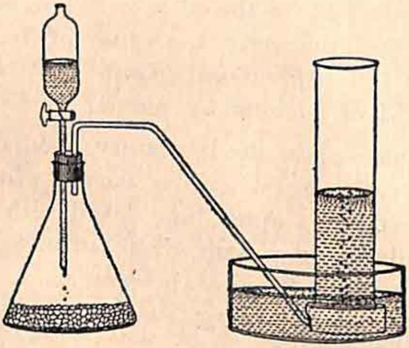


Fig. 20. Preparation of methane from methyl iodide.

The gas is more cheaply made likewise from aluminium carbide and water.

$$\underset{\text{Aluminium carbide}}{Al_4C_3} + 12H_2O = 4Al(OH)_3 + \underset{\text{Methane}}{3CH_4}.$$

Two other methods, of theoretical importance, are:

(*iii*) By passing carbon monoxide or dioxide over finely-divided nickel with hydrogen at about 200°:

$$CO + 3H_2 = CH_4 + H_2O.$$

(*iv*) By maintaining an electric arc between carbon poles in an atmosphere of hydrogen:

$$C + 2H_2 = CH_4.$$

Properties.—Methane is an odourless and colourless gas, lighter than air and sparingly soluble in water. It burns in air with a non-luminous flame (but forms an explosive mixture with air) producing CO_2 and water:

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Methane is a very stable compound, being unaffected by acids, alkalis, oxidising or reducing agents, etc. This is characteristic of all paraffins. Chlorine, however, acts slowly on it in diffused day-light, replacing hydrogen one by one:

$$CH_4 + Cl_2 = \underset{\text{Methyl chloride}}{CH_3Cl} + HCl.$$

$$CH_3Cl + Cl_2 = \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl.$$

$$CH_2Cl_2 + Cl_2 = \underset{\text{Chloroform}}{CHCl_3} + HCl.$$

$$CHCl_3 + Cl_2 = \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl.$$

The process is known as *substitution*. Bromine gives similar products but iodine is without action.

In U.S.A. natural gas is used as a fuel and also for making carbon black by *incomplete* combustion. Two very important products, methyl alcohol and formaldehyde, are made from methane by *partial* oxidation.

$$2CH_4 + O_2 = \underset{\text{Methyl alcohol}}{2CH_3OH}. \qquad CH_4 + O_2 = \underset{\text{Formaldehyde}}{HCHO} + H_2O.$$

Ethane, C_2H_6.—With methane, ethane or dimethyl occurs in natural gas as well as coal-gas.

Preparation.—(*i*) By heating sodium propionate with soda-lime (*cf.* methane):

$$\underset{\text{Sodium propionate}}{CH_3.CH_2.COONa} + NaOH = \underset{\text{Ethane}}{C_2H_6} + Na_2CO_3.$$

(*ii*) By reacting zinc-copper couple in presence of alcohol with ethyl iodide:

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H = \underset{\text{Ethane}}{C_2H_6} + HI.$$

(*iii*) By treating methyl iodide in *dry* ether solution with metallic sodium in thin slices (*Wurtz Reaction*).

$$\underset{\text{Methyl iodide}}{CH_3}|\overline{I + 2Na + I}|CH_3 = 2NaI + \underset{\text{Ethane}}{C_2H_6}.$$

(*iv*) By passing electric current through a concentrated solution of sodium acetate in water ; ethane and CO_2 appear at the anode (*Kolbe's synthesis*).

$$\underset{\text{Sodium acetate}}{\begin{array}{l|l|l} CH_3 & COO & Na \\ CH_3 & COO & Na \end{array}} + 2H_2O = \underset{\text{Ethane}}{C_2H_6} + 2CO_2 + H_2 + 2NaOH.$$

(*v*) A mixture of ethylene and hydrogen, passed over finely-divided nickel at high temperature, gives ethane:

$$\underset{\text{Ethylene}}{C_2H_4} + H_2 = C_2H_6.$$

Properties.—Ethane strikingly resembles methane in its properties—being a colourless and odourless gas, practically insoluble in water. It is very stable and inert chemically but reacts with chlorine like methane giving similar substitution products:

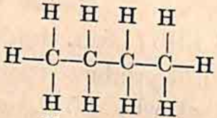
$$\underset{\text{Ethane}}{C_2H_6} \xrightarrow{Cl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} \longrightarrow \underset{\text{Dichloro-ethane}}{C_2H_4Cl_2} \longrightarrow \underset{\text{Trichloroethane}}{C_2H_3Cl_3} \longrightarrow$$

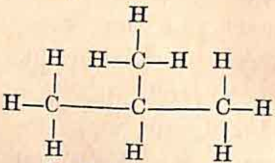
$$\underset{\text{Tetrachloroethane}}{C_2H_2Cl_4} \longrightarrow \underset{\text{Pentachloroethane}}{C_2HCl_5} \longrightarrow \underset{\text{Hexachloroethane}}{C_2Cl_6}.$$

Propane, C_3H_8, and *butane*, C_4H_{10}, are the next members of the paraffin family, having similar properties. There are many more. If all these hydrocarbons are arranged in order of their increasing mol. wt., it is found that they form an arithmetical progression with the common difference CH_2, *i.e.*, each member differs from its succeeding or preceding one by a $-CH_2-$ group. The saturated hydrocarbons can be expressed by the general molecular formula, C_nH_{2n+2}, where n is an integer. As we ascend the series, we find a regular gradation of physical properties such as b.p., m.p., sp. gr., solubility, etc. Their chemical properties are strikingly similar. Such a series of closely related compounds is known as *homologous series*, and the individual members as *homologues*. In other classes of compounds such series exists and when we know one member of a family, we can foretell more or less accurately the behaviour of others. This has made the study of such a large number of organic compounds rather easy and interesting. It would be impossible to remember thousands of organic compounds if they all had different characteristics.

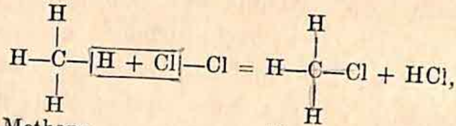
Petroleum.—The most important natural source of the paraffins is petroleum (*petra,* rock ; *oleum,* oil) or mineral oil which occurs in many countries, notably in the U.S.A., Persia, Russia and Iraq ; comparatively small amounts exist in Burma, Assam and other places. In 1946 U.S.A. produced 174·87 crores barrels (62·5% of the world production) while India produced only 2·27 lacs barrels of which 75% came from Assam (1 barrel = 42 gallons). The oil is pumped out through bore-holes, sometimes 5,000—15,000 ft. deep, and led through long pipes, some of which are 1,700 miles long, to the refinery on the sea-coast. The oil is distilled into fractions of different boiling points such as petrol ether, petrol, benzine, kerosene, lubricating oil, vaseline, paraffin wax, etc. The most important fraction is, however, petrol required for motor cars and aeroplanes. American oils consist mainly of paraffins but Russian oils contain naphthenes which are hydrocarbons of another type. Paraffin wax is used in making candles ; benzine for dry cleaning, vaseline in ointments and petrol ether for oil extraction. The residue after distillation is pitch, used in road-making. Synthetic rubber, plastics, glycerine, alcohol, and a host of organic compounds are now derived from petroleum.

Isomerism and structural formula.—In the paraffin family there are *two* small members having the *same* molecular formula, C_4H_{10}, named butane and iso-butane, having somewhat different properties. Since they are different compounds but have the same formula, the arrangement of the atoms inside the molecules must be different. The nature and number of atoms in the molecule cannot alone give a full picture of the compounds. Compounds having the same molecular formula but different properties, are known as *isomers* (*isos,* equal; *meros,* part) and the phenomenon is called *isomerism.* C_5H_{12} represents three isomers; C_6H_{14} does 5, while C_9H_{20} has 35. Normal butane and iso-butane have the structural formulæ (straight-chain isomers are called *normal* isomers):


Normal butane


Iso-butane

This graphical representation, based upon chemical and physical evidences, is termed *structural formula* or *constitution* of a compound. The behaviour of an organic compound can be largely explained by its constitution. Organic reactions can be better understood when expressed in terms of structural changes. For example, the action of chlorine on methane is easier to follow when represented as



$$H\text{—}\underset{H}{\overset{H}{C}}\text{—}\boxed{H + Cl}\text{—}Cl = H\text{—}\underset{H}{\overset{H}{C}}\text{—}Cl + HCl,$$

Methane Methyl chloride

one hydrogen atom being replaced by chlorine.

Methyl chloride, CH_3Cl, may exchange its reactive chlorine atom for other groups such as $-NO_2$, $-OH$, $-CN$, etc. giving nitro-methane, CH_3NO_2, methyl alcohol, CH_3OH, methyl cyanide, CH_3CN, etc. in which the group or *radical,* $-CH_3$, remains intact, and behaves more or less like ammonium, $-NH_4$, in inorganic compounds. Such radicals are incapable of independent existence for long. The methyl radical, $-CH_3$, is monovalent; other similar radicals are ethyl, $-C_2H_5$, propyl, $-C_3H_7$, butyl, $-C_4H_9$, etc.; these are generally called *alkyl radicals.*

The names of paraffins end in '*-ane*' as those of metals end in '-um'; *e.g.,* methane, ethane, propane, butane, pentane, hexane, heptane, and so on. The alkyl groups or radicals corresponding to these are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and so on. This nomenclature or naming helps recognising the members as in a human family.

Questions

1. Describe the method of preparation of ethane. From ethane how would you obtain ethylene and acetylene? Compare the properties of the three hydrocarbons. I.Sc., 1952, Nagpur Uni.
2. Write short notes on: isomerism, homologous series, structural formula, and alkyl radical, giving examples in each case.
3. What is a paraffin? Why is it so called? What is Wurtz method for preparing paraffins?
4. What is petroleum? What important fractions is it distilled into? What are their uses?

CHAPTER V

Unsaturated hydrocarbons.—Hydrocarbons that contain double or triple bonds, *i.e.,* have proportionately less hydrogen than the corresponding paraffins, are called unsaturated hydrocarbons. There are two important families *viz. ethylenes, alkenes,* or *olefines,* C_nH_{2n}, and *alkynes,* or *acetylenes,* C_nH_{2n-2}. The first member of the ethylene series is ethylene, C_2H_4.

Ethylene, C_2H_4.—It occurs in coal gas (3-4% by volume) and makes the flame luminous. Natural gas of U.S.A. contains about 20% of ethylene.

Preparation.—In the laboratory, ethylene is usually prepared by heating ethyl alcohol with *excess* of conc. H_2SO_4, or syrupy phosphoric acid, both of which are strong dehydrating agents and abstract the elements of water from the alcohol. The reaction occurs in two stages.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} = \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 = \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

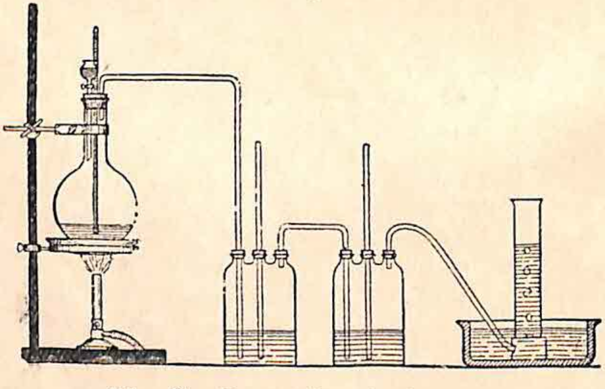


Fig. 21. Preparation of ethylene

Alcohol and thrice its volume of conc. H_2SO_4 are taken in the flask and heated to about 165° on a sand-bath. The issuing gas is purified by passing through gas-washers containing caustic potash and collected over water. When the reaction slackens, a fresh mixture of alcohol and H_2SO_4 is slowly run in from the tap-funnel. The gas is not, however, pure.

(*ii*) Pure ethylene may be made by reacting hot alcoholic potash with ethyl iodide, or by the action of zinc on warm ethylene dibromide dissolved in alcohol. The yield in the first case is poor (less than 1%) due to formation of ether. The function of alcoholic KOH is to remove one molecule of halogen hydracid such as HI. Aqueous KOH and ethyl iodide give ethyl alcohol, C_2H_5OH.

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + KOH\ (\text{alc.}) = \underset{\text{Ethylene}}{C_2H_4} + KI + H_2O.$$

$$\underset{\text{Ethylene dibromide}}{C_2H_4Br_2} + Zn = \underset{\text{Ethylene}}{C_2H_4} + ZnBr_2.$$

(*iii*) By passing alcohol vapour over alumina, Al_2O_3, at about 360°, ethylene is obtained in high yield.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} = \underset{\text{Ethylene}}{C_2H_4} + H_2O.$$

Properties.—Ethylene is a colourless gas with a faint sweetish smell. It is sparingly soluble in water but more soluble in alcohol. On prolonged inhalation of the gas, people become unconscious. It burns in air with a luminous flame, producing CO_2 and water.

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O,$$

but forms an explosive mixture with air. Unlike paraffins, it is reactive, most of its reactions being additive.

(*i*) Hydrogen, at about 150° and in presence of catalysts like platinum black or palladium, is added up and an *addition compound*, ethane, results. Nascent hydrogen, from zinc and H_2SO_4 for example, cannot reduce ethylene to ethane.

$$\underset{\text{Ethylene}}{C_2H_4} + H_2 = \underset{\text{Ethane}}{C_2H_6}.$$

(*ii*) Ethylene combines readily with halogens in presence of light producing ethylene halides.

$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$
Ethylene Ethylene dichloride (Dutch liquid)

The liquid is oily; five Dutch chemists who discovered ethylene, named it *olefiant* or oil-forming gas; 'olefines' now stands for ethylene and its homologues.

(*iii*) With halogen hydracids, *e.g.*, HI, ethylene forms ethyl halides by addition.

$$C_2H_4 + HI = C_2H_5I.$$
Ethylene Ethyl iodide

(*iv*) With hypochlorous acid, it forms ethylene chlorhydrin, a colourless liquid:

$$C_2H_4 + HClO = C_2H_4(Cl)\,(OH).$$
Hypochlorous acid Ethylene chlorhydrin

(*v*) With conc. H_2SO_4, it produces ethyl hydrogen sulphate, which on boiling with dilute acids, gives ethyl alcohol. In the second stage, water brings about the change; so it is called *hydrolysis.*

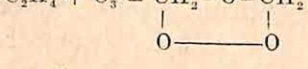
$$C_2H_4 + H_2SO_4 = C_2H_5.SO_4H.$$
Ethylene Ethyl hydrogen sulphate

$$C_2H_5SO_4H + H_2O = C_2H_5OH + H_2SO_4.$$
Ethyl hydrogen sulphate Ethyl alcohol

(*vi*) With a dilute alkaline solution of potassium permanganate, it forms ethylene glycol in the cold.

$$C_2H_4 + H_2O + O = C_2H_4(OH)_2.$$
Ethylene glycol

(*vii*) Ethylene unites with ozone giving an unstable ozonide:

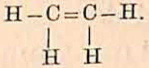


$$C_2H_4 + O_3 = \begin{array}{c} CH_2-O-CH_2 \\ |\qquad\quad| \\ O\text{———}O \end{array}$$

Uses.—Ethylene from natural gas is converted into alcohol. The gas is employed for artificial ripening of green fruits such as banana and also as an anæsthetic.

Structure.—From analytical data, the molecular formula of ethylene is C_2H_4. It is formed from ethyl alcohol,

C_2H_5OH. By catalytic hydrogenation, ethylene gives ethane, C_2H_6. In both ethane and ethyl alcohol, the two carbon atoms are known to be directly linked. Since carbon is tetravalent, ethylene is represented as



$$H-\underset{\displaystyle H}{\underset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}-H.$$

This is supported by the facts that free valency bonds do not exist, and whenever ethylene reacts, it takes up *two* monovalent atoms or groups. This double linkage or bond must not, however, be assumed to be twice as strong as a single valency bond between carbon atoms; just the opposite is correct. Double or triple bonds produce a 'strain' in the molecule—the normal directions of the valency bonds are thus changed (Fig. 22). Such compounds are consequently less stable and so more reactive than the paraffins.

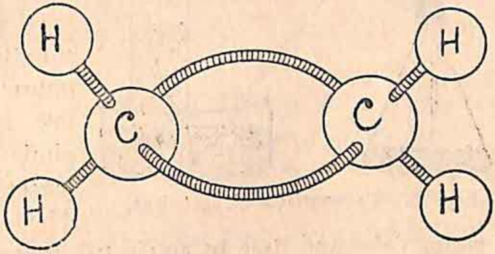
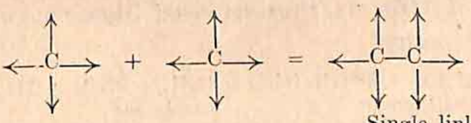


Fig. 22. Double linkage (Ethylene).



Single linkage

Acetylene, C_2H_2.—Still more unsaturated and much more unstable or reactive than ethylene is the hydrocarbon, acetylene which contains a triple bond. It does not occur in nature, coal-gas contains only traces of it. The gas was accidentally discovered by an American who wanted to prepare metallic calcium by reducing its oxide with carbon in an electric furnace ; by pouring the resulting mass into a bucket of water, he got acetylene but no calcium. Acetylene is formed when a Bunsen burner 'strikes back.'

Preparation.—The best way of preparing acetylene is to add water to calcium carbide :

$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O = Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}.$$

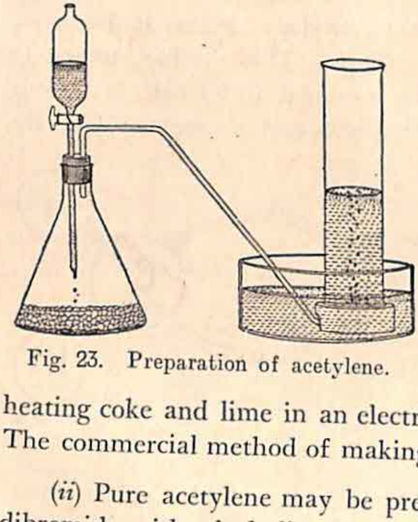


Fig. 23. Preparation of acetylene.

Small lumps of carbide are taken in the flask and water added slowly from the separating funnel. The gas is collected over water. It contains sulphuretted and phosphoretted hydrogen coming from calcium sulphide and phosphide present in the carbide. The carbide is made by heating coke and lime in an electric furnace at about 3000°. The commercial method of making acetylene is the same.

(*ii*) Pure acetylene may be prepared by boiling ethylene dibromide with alcoholic potash (*cf*. ethylene. p. 35). Two molecules of HBr are thus removed from one molecule of ethylene bromide.

$$\underset{\text{Ethylene dibromide}}{C_2H_4Br_2} + 2KOH\ (\text{alc.}) = \underset{\text{Acetylene}}{C_2H_2} + 2KBr + 2H_2O.$$

Since ethyl alcohol and H_2SO_4 give ethylene, and the latter with bromine yields ethylene dibromide, acetylene may be obtained from ethyl alcohol.

(*iii*) By striking an electric arc between carbon poles in an atmosphere of hydrogen, acetylene may be obtained from its elements but the yield is very poor.

$$2C + H_2 = C_2H_2.$$

Properties.—Acetylene is a colourless gas with a pleasant smell when pure, and fairly soluble in water. It can be liquefied but the liquid is highly explosive; so it cannot be transported in liquid form like ammonia or sulphur dioxide. Acetone, an organic solvent, dissolves under pressure about 300 times its own volume of acetylene. The gas is usually sold in acetone solution. On releasing the pressure, almost all the gas comes out. It burns in air with a smoky flame (but forms, like ethylene, an explosive mixture with air), the gas, however, produces a dazzling flame when burnt in special pin-hole burners as is done in the country-side. When acetylene burns in oxygen, the flame has a very high temperature, something like 3500°, at which almost all metals melt. Oxy-acetylene burners are, therefore, used in welding and cutting of metals.

Reactions.—(*i*) By catalytic hydrogenation (finely-divided nickel or platinum black is generally employed) acetylene first forms ethylene and then ethane, at ordinary temperature (*cf. ethylene* p. 35). This and the following, except (iv & v), are all *addition reactions,* characteristic of unsaturated compounds.

$$\underset{\text{Acetylene}}{C_2H_2} \xrightarrow{2H} \underset{\text{Ethylene}}{C_2H_4} \xrightarrow{2H} \underset{\text{Ethane}}{C_2H_6}.$$

(*ii*) Chlorine reacts with the gas violently, producing HCl and carbon:

$$\underset{\text{Acetylene}}{C_2H_2} + Cl_2 = 2HCl + 2C.$$

Bromine reacts less vigorously, giving the tetrabromide finally:

$$\underset{\text{Acetylene}}{C_2H_2} \xrightarrow{Br_2} \underset{\text{Acetylene dibromide}}{C_2H_2Br_2} \xrightarrow{Br_2} \underset{\text{Acetylene tetrabromide}}{C_2H_2Br_4}.$$

(*iii*) With HBr, acetylene forms additive compounds—first vinyl bromide and finally, ethylidene bromide.

$$\underset{\text{Acetylene}}{C_2H_2} \xrightarrow{HBr} \underset{\text{Vinyl bromide}}{CH_2{=}CHBr} \xrightarrow{HBr} \underset{\text{Ethylidene bromide}}{CH_3CHBr_2}.$$

(*iv*) Passed into ammoniacal solution of silver or copper salts, acetylene, unlike ethane and ethylene, forms acetylides, Ag_2C_2 or Cu_2C_2. This is utilised for detecting the gas as the copper compound is red, and insoluble in water. Calcium carbide, CaC_2, is really calcium acetylide.

(*v*) At dull red heat, three of its molecules coalesce and form benzene, one of the most important organic compounds. The yield is poor.

$$\underset{\text{Acetylene}}{3C_2H_2} = \underset{\text{Benzene}}{C_6H_6}.$$

Such a process which involves the union of two or more molecules of a substance to form a new and more complex one, is known as *polymerisation*. The polymer (benzene in this case) has the same percentage composition as, but a higher mol. wt. than, the original compound. The relationship is called *polymerism*.

(*vi*) Passed into warm, dilute H_2SO_4 containing a little mercuric sulphate, acetylene takes up a molecule of water and forms acetaldehyde, CH_3CHO.

$$C_2H_2 + H_2O = CH_3CHO.$$

Uses.—Acetylene is largely used for welding and cutting metals, as an illuminant, for making synthetic rubber and also as an anæsthetic. Acetaldehyde, acetic acid and ethyl alcohol are made from acetylene in some countries.

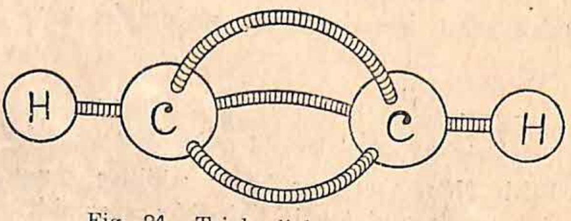


Fig. 24. Triple linkage (Acetylene).

The greater instability of acetylene, compared with ethylene, is due to the existence of a triple bond between the carbon atoms; this produces a much greater strain in the molecule due to the deflection of normal valency bonds (vide Fig. 24). Acetylene has the structure, $CH \equiv CH$.

Questions

1. Give methods for preparing ethylene. Give its physical and chemical properties. How will you write the structural formula of this compound? Give reasons for your answer.
I.Sc. 1951, Nagpur Uni.

2. How is acetylene prepared? What are its properties? How would you distinguish between ethane, ethylene and acetylene?
I.Sc., 1955, Nagpur Uni.

3. Illustrate with examples: polymerisation, hydrolysis, substitution products, and addition products.

CHAPTER VI

Halogen derivatives of paraffins.—As already mentioned, paraffins react with Cl_2 and Br_2 to form alkyl halides. From methane, CH_4, for example, all the four hydrogen atoms can be replaced, one by one, by Cl_2. This method of direct halogenation is slow, and a mixture of halogenated paraffins is thus obtained; these are difficult to separate. There are more suitable methods for their preparation. The mono-halogen derivatives of the paraffins, *i.e.*, alkyl halides, are important as unlike the paraffins, they are quite reactive and can be converted into various other compounds.

Methods of preparing alkyl halides.—(*i*) By direct halogenation of paraffins:

$$\underset{\text{Methane}}{CH_4} + Cl_2 = \underset{\text{Methyl chloride}}{CH_3Cl} + HCl.$$

Alkyl iodides cannot be prepared by the action of iodine alone as HI formed reduces them back to paraffins:

$$\underset{\text{Methane}}{CH_4} + I_2 \rightleftarrows \underset{\text{Methyl iodide}}{CH_3I} + HI.$$

In presence of iodic acid, HIO_3, or mercuric oxide, HgO, however, the back reaction cannot occur due to the removal of HI.

(*ii*) By the action of phosphorus halides on alcohols, alkyl halides are readily obtained in good yield. Alcohols are hydroxy-compounds of paraffins; methyl alcohol is CH_3OH, ethyl alcohol has the molecular formula, C_2H_5OH and so on. Phosphorus tri- or penta-chloride may be used for preparing alkyl halides. With methyl alcohol, it gives methyl chloride, CH_3Cl; with ethyl alcohol, we get ethyl chloride, C_2H_5Cl. The function of PCl_3 or PCl_5 is to replace the hydroxyl group, —OH, of the alcohols by chlorine; the reaction is a general one.

$$\underset{\text{Ethyl alcohol}}{3C_2H_5OH} + PCl_3 = \underset{\text{Ethyl chloride}}{3C_2H_5Cl} + \underset{\text{Phosphorous acid}}{H_3PO_3}.$$

$$C_2H_5OH + PCl_5 = C_2H_5Cl + \underset{\text{Phosphorus oxychloride}}{POCl_3} + HCl.$$

To prepare alkyl bromides and iodides, the corresponding phosphorus halides are made *in situ* by treating a mixture of red phosphorus and bromine or iodine with the alcohol.

Preparation of ethyl bromide.—As a typical example, let us see how ethyl bromide is prepared in the laboratory. Any alkyl bromide can thus be prepared. By using iodine in place of bromine, we get alkyl iodides.

Ethyl alcohol (75 c.c.) dried over quicklime, and red phosphorus (15 g.) are taken in a distilling flask and bromine (20 c.c.) in a tap-funnel. The flask is placed on a water-bath and connected through a condenser to a receiver which again is connected with a soda-lime tower. The soda-lime absorbs the fumes of HBr formed. Bromine is added *drop by drop* and the reaction mixture is allowed to stand for some hours after all the bromine has been added. The contents are then distilled, replacing the tap-funnel by a thermometer; the distillate upto 60° is collected. This contains ethyl bromide, HBr and alcohol. The latter two are removed by aqueous sodium carbonate and the residual water by shaking with fused $CaCl_2$. It is re-distilled to obtain pure ethyl bromide.

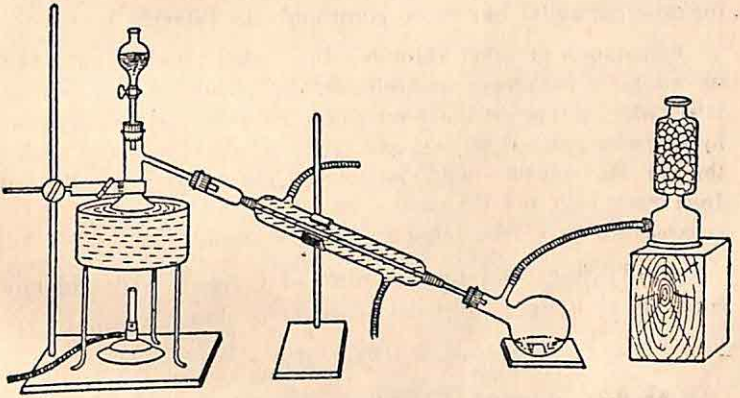
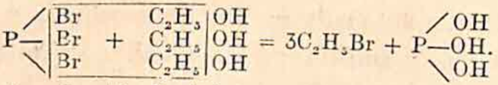


Fig. 25. Preparation of ethyl bromide.

$$P_4 + 6Br_2 = 4PBr_3.$$



$$P\begin{cases}Br\\ Br\\ Br\end{cases} + \begin{array}{l|l}C_2H_5 & OH\\ C_2H_5 & OH\\ C_2H_5 & OH\end{array} = 3C_2H_5Br + P\begin{cases}OH\\ OH.\\ OH\end{cases}$$

Phosphorus bromide Ethyl alcohol Ethyl bromide Phosphorous acid

(*iii*) Alkyl halides are conveniently prepared by the action of halogen hydracids such as HCl, HBr, etc. on alcohols in presence of H_2SO_4 or $ZnCl_2$ which removes the water formed, so that the opposite reaction does not occur.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + HCl \Longleftrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O.$$

This recalls the neutralisation of a caustic alkali with an acid; alkyl halides are, therefore, regarded as alkyl salts (or ethereal salts) but more commonly as *esters*.

Preparation of ethyl chloride.—Dry ethyl alcohol and half its weight of anhydrous zinc chloride, $ZnCl_2$, are taken in a flask fitted with an upright condenser and a side-tube. HCl gas, made by dropping conc. H_2SO_4 on conc. HCl, is passed into the alcohol through the side-tube until saturated. The contents are distilled from water-bath and the issuing gas (ethyl chloride boils at 12·5°) is condensed in a tube cooled by freezing mixture.

(*iv*) Olefines add up one mol. of halogen hydracid and form alkyl halides. But the reaction is slow.

$$\underset{\text{Ethylene}}{CH_2=CH_2} + HBr = \underset{\text{Ethyl bromide}}{CH_3—CH_2Br.}$$

Methyl chloride, CH_3Cl, is best prepared, like ethyl chloride, by the action of HCl gas on *dry* methyl alcohol, CH_3OH, in presence of conc. H_2SO_4 or zinc chloride. It is a colourless gas with a sweet smell, insoluble in water. It is readily soluble in alcohol. Methyl chloride is a fire extinguisher and a local anæsthetic in minor surgical operations. It is sometimes employed as a cooling agent in refrigerators.

Ethyl chloride, C_2H_5Cl, is also a colourless gas, insoluble in water. Like methyl chloride, it is a local anæsthetic.

The liquid lowers the temperature by very quick evaporation. The effect is, however, short-lived.

Methyl bromide, CH_3Br, a gas (b.p. 4·5°), is stored in æroplanes in liquid form for use as a fire extinguisher.

Ethyl bromide, C_2H_5Br, is a colourless liquid boiling at 38·5° ; it has a sweet odour which, as we shall see later on, is characteristic of all esters.

Methyl iodide, CH_3I, is a colourless liquid, boiling at 45°. It is used to introduce a methyl group, CH_3—, in organic compounds, being more reactive than methyl chloride.

Ethyl iodide, C_2H_5I, is also a colourless liquid (b.p. 72·8°). Reactions of ethyl iodide are noted below, other alkyl halides behave more or less similarly.

Reactions of ethyl iodide, C_2H_5I.— (1) By reduction with nascent hydrogen (from zinc and HCl) it forms ethane:

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H = \underset{\text{Ethane}}{C_2H_6} + HI.$$

(2) Aqueous KOH or *moist* silver oxide produces ethyl alcohol, iodine is replaced by -OH group.

$$\underset{\text{Ethyl iodide}}{C_2H_5|\overline{I + K}|OH} \text{ (aq.)} = \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KI.$$

Moist silver oxide, Ag_2O, behaves like silver hydroxide, AgOH.

Alcoholic KOH, however, gives mainly ether, and only a little ethylene:

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KOH \text{ (alc.)} = \underset{\text{Ether}}{C_2H_5.O.C_2H_5} + KI + H_2O.$$

$$C_2H_5I + KOH \text{ (alc.)} = \underset{\text{Ethylene}}{C_2H_4} + KI + H_2O.$$

(2) Metallic sodium produces butane with ethyl iodide in ether solution (*Wurtz Reaction*).

$$\underset{\text{Ethyl iodide}}{C_2H_5|\overline{I + 2Na + I}|C_2H_5} = \underset{\text{Butane}}{C_2H_5{-}C_2H_5} + 2NaI.$$

(4) With silver nitrite, nitro-ethane is obtained:

$$C_2H_5\boxed{I + Ag}NO_2 = \underset{\text{Nitro-ethane}}{C_2H_5.NO_2} + AgI.$$

(5) On heating ethyl iodide with ammonia dissolved in alcohol, ethylamine is obtained, iodine being replaced by an amino group, $-NH_2$.

$$C_2H_5\boxed{I + H}\underset{\text{Ammonia}}{NH_2}(alc.) = \underset{\text{Ethylamine}}{C_2H_5NH_2} + HI.$$

(6) Ethyl cyanide results when ethyl iodide and potassium cyanide in alcohol are heated together; iodine is substituted by a cyanogen group, -CN.

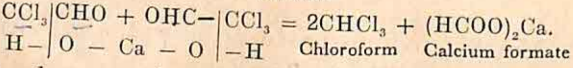
$$C_2H_5\boxed{I + K}CN = \underset{\text{Ethyl cyanide}}{C_2H_5CN} + KI.$$

There are good many other halogen derivatives of the paraffins; of these, the most important are chloroform, iodoform and carbon tetrachloride.

Chloroform, trichloromethane, $CHCl_3$, is formed when Cl_2 acts on methane (p. 29). In the laboratory or in the factory, it is made by distilling a mixture of ethyl alcohol (or acetone), water and bleaching powder. The reaction is rather complex, and takes place in several steps. Alcohol is first oxidised to acetaldehyde by chlorine coming from bleaching powder; chlorine chlorinates acetaldehyde to trichloroacetaldehyde or chloral which finally yields chloroform by hydrolysis with slaked lime, derived from the bleaching powder.

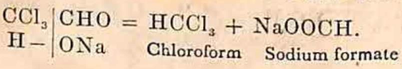
(*i*) $\underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} + Cl_2 = \underset{\text{Acetaldehyde}}{CH_3.CHO} + 2HCl.$

(*ii*) $CH_3.CHO + 3Cl_2 = \underset{\text{Chloral}}{CCl_3.CHO} + 3HCl.$

(*iii*) 

$$\begin{array}{l|l|l} CCl_3 & CHO + OHC- & CCl_3 \\ H- & O - Ca - O & -H \end{array} = \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}.$$

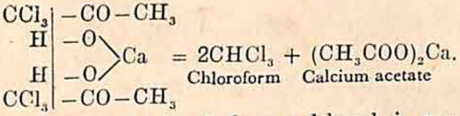
Chloral reacts with caustic soda and gives chloroform.



$$\begin{array}{l|l} CCl_3 & CHO \\ H- & ONa \end{array} = \underset{\text{Chloroform}}{HCCl_3} + \underset{\text{Sodium formate}}{NaOOCH}.$$

With acetone, trichloro-acetone is first formed, which reacts with slaked lime to give chloroform as does chloral.

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 3Cl_2 = \underset{\text{Trichloro-acetone}}{CCl_3.CO.CH_3} + 3HCl.$$



$$\left.\begin{array}{l|l} CCl_3 & -CO-CH_3 \\ H & -O \\ H & -O \\ CCl_3 & -CO-CH_3 \end{array}\right\rangle Ca = \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca}.$$

Chloroform obtained from chloral is much purer than that from alcohol or acetone, and so is used in surgery.

(*ii*) By passing an electric current through a 20% solution of common salt, NaCl, in aqueous acetone or alcohol, chloroform is manufactured in U.S.A.

Properties.—Chloroform is a heavy (sp. gr. 1·5), colourless and non-inflammable liquid with a pleasant smell. It boils at 61°, is insoluble in water but readily soluble in alcohol or ether. It is extensively used as an anæsthetic in surgical operations, usually mixed with ether for better results. On exposure to light, chloroform suffers decomposition, one of the products being phosgene or carbonyl chloride, $COCl_2$, which is very poisonous.

$$2CHCl_3 + O_2 = 2HCl + 2COCl_2$$

To arrest this decomposition, chloroform is usually stored in bottles of amber colour, full to the neck, and mixed with about 1% of alcohol. On heating with NaOH, chloroform gives sodium formate:

$$CHCl_3 + 4NaOH = \underset{\text{Sodium formate}}{H.COONa} + 3NaCl + 2H_2O$$

A sensitive test for chloroform is to warm a few drops of it with a drop of aniline and a little alcoholic potash; an intolerable smell of phenyl isocyanide is at once perceptible.

$$\underset{\text{Chloroform}}{CHCl_3} + 3KOH + \underset{\text{Aniline}}{C_6H_5NH_2} = \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

Spirit chloroform is used in medicine as a hypnotic. Chloroform is an excellent solvent for resins and oils, and widely used as an industrial solvent.

Iodoform, CHI_3, is important as an antiseptic. It is made by the action of iodine and caustic soda (or sodium carbonate) on alcohol or acetone. The mechanism of the reaction is similar to that of chloroform.

$$4I_2 + 6NaOH + \underset{\text{Ethyl alcohol}}{C_2H_5OH} = \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium formate}}{HCOONa} + 5NaI + 5H_2O.$$

By passing an electric current through a dilute, warm alcoholic or acetone solution of potassium iodide containing sodium carbonate, iodoform is made commercially.

Iodoform is a pale yellow, crystalline solid (m. p. 119°) with a strong, unpleasant smell. It is insoluble in water but dissolves in warm alcohol. It sublimes readily and so can be easily purified. On heating with NaOH, iodoform splits up, like chloroform, into sodium formate, etc.

$$\underset{\text{Iodoform}}{CHI_3} + 4NaOH = \underset{\text{Sodium formate}}{HCOONa} + 3NaI + 2H_2O.$$

You can readily make iodoform as follows. Take sodium carbonate (3 g.) and water (10 c.c.) in a test-tube and warm. Add alcohol (2 c.c.) and iodine (1 g.) slowly and shake. Yellow ppt. of iodoform appears almost immediately.

Carbon tetrachloride, CCl_4, is the final product of direct chlorination of methane (p. 29) but it is never made like that. It is an important industrial solvent and is usually manufactured by chlorinating carbon disulphide in presence of a catalyst, *e.g.* manganese chloride or aluminium chloride. It is purified by fractional distillation.

$$\underset{\text{Carbon disulphide}}{CS_2} + 3Cl_2 = \underset{\substack{\text{Sulphur}\\\text{chloride}}}{S_2Cl_2} + \underset{\substack{\text{Carbon}\\\text{tetrachloride}}}{CCl_4}.$$

Carbon tetrachloride is a colourless, non-inflammable, heavy liquid (b.p. 76°) with a sweetish odour. It is largely employed for the extraction of fats and oils, in dry cleaning and a solvent for grease. It is a fire extinguisher (trade name *pyrene*). Hot alcoholic potash decomposes carbon tetrachloide as

$$CCl_4 + 6KOH = 4KCl + 3H_2O + K_2CO_3.$$

Questions

1. Give the method of preparation and mention the properties of chloroform. Starting from chloroform how would you obtain carbon tetrachloride and formic acid? I.Sc. 1952, Nagpur Uni.

2. Describe the preparation of ethyl iodide. How is it used in organic synthesis? I.Sc. 1954, Bombay Uni.

3. Write down the structural formulae for ethyl chloride, nitroethane, ethylamine, ethyl cyanide, sodium formate and iodoform.

4. How is carbon tetrachloride manufactured? What are its chief uses?

CHAPTER VII

Alcohols.—When one or more hydrogen atoms of the paraffins are replaced by a corresponding number of hydroxyl groups, we get a series of compounds known as *alcohols*. They are, therefore, hydroxy-paraffins. Alcohols with only one hydroxyl group are called monohydric alcohols, with two, dihydric alcohols, with three, trihydric alcohols. Those containing more than one hydroxyl group are, however, generally termed polyhydric alcohols. Examples are methyl alcohol, CH_3OH (monohydric), ethylene glycol, $HOCH_2$-CH_2OH (dihydric), glycerol, $HOCH_2$-CHOH-CH_2OH (trihydric). It is extremely rare to find *two* or more -OH groups attached to the *same* carbon atom; water eliminates in such cases and new types of compounds result. Common alcohol is ethyl alcohol, C_2H_5OH.

Alcohols are *primary, secondary* or *tertiary* according as they contain the groups $-CH_2OH$, $=CHOH$ or $\equiv COH$ in their molecules. Thus methyl alcohol, CH_3OH, is a primary alcohol; isopropyl alcohol, $CH_3.CHOH.CH_3$, is a secondary alcohol while tertiary butyl alcohol is $(CH_3)_3COH$.

Alcohols are usually named according to the hydrocarbon radical to which the hydroxyl group is linked, *e.g.*, methyl alcohol, CH_3-OH; ethyl alcohol, C_2H_5-OH, and so on. Another way is to add '-ol' for '-e' to the name of paraffins, *e.g.*, methanol, CH_3OH; ethanol, C_2H_5OH, butanol, C_4H_9OH, and so on.

Putting R for the alkyl group, monohydric alcohols have the general formula R.OH. Of these, by far the most important is ethyl alcohol, so much so that it is known simply as alcohol; the first member of the series is methyl alcohol.

Methyl alcohol, methanol, CH_3OH, occurs in oil of winter-green in combined state. It is also called wood-spirit or wood-naphtha and made by the following two methods.

(i) Synthetic process.—By passing purified water gas (made by leading steam over red-hot coke) with half its volume of hydrogen under pressure (200-600 atmospheres) over a catalyst (zinc and chromium oxides) at 350°-400°, most of the methanol of commerce is manufactured. The conversion is about 25%.

$$\underset{\text{Water gas}}{(CO + H_2)} + H_2 \rightleftharpoons \underset{\text{Methyl alcohol}}{CH_3OH.}$$

(ii) By distillation of wood.—When air-dried wood is heated in iron retorts, out of contact with air, at about 350° for some 30 hours, we obtain (1) wood gas (containing methane, CO_2, H_2, etc.), (2) an aqueous distillate called 'pyroligneous acid' (*pyro*, fire; *lignum*, wood) (containing 2-4% methyl alcohol, about 10% acetic acid, water and a little acetone), (3) wood tar and (4) charcoal. To separate methyl alcohol, pyroligneous acid is boiled and the vapour led into hot milk of lime. Acetic acid is retained as non-volatile calcium acetate, and acetone and methyl alcohol with water pass over. The condensed mixture is then fractionally distilled; most of the acetone (b.p. 56°) goes over, the residual liquid is dried over quicklime and re-distilled to obtain moderately pure (about 98%) wood-spirit (b.p. 64°).

In 1948 U.S.A. made 155 million gallons of synthetic methanol and only 2·5 million gallons of wood-spirit, the former more cheaply.

Properties.—Methyl alcohol is a colourless liquid (b.p. 64°), lighter than water (sp. gr. 0·8) and miscible with it in all proportions. It has a pleasant smell, a burning taste and is poisonous. Methanol is, therefore, employed to denature ethyl alcohol (in making methylated spirit) to render it unfit for drinking. All wines contain ethyl alcohol; these are taxed by the government.

On oxidation, methanol finally gives CO_2:

$$\underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{O} \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{O} \underset{\text{Formic acid}}{HCOOH} \xrightarrow{O} CO_2.$$

These stages of oxidation should be noted; *all* primary alcohols behave likewise—they first take up one atom of oxygen and generally pass on to aldehydes (compounds containing a $-CHO$ group attached to the hydrocarbon radical, *i.e.*, $R-CHO$). The latter combine with another oxygen atom and form acids (compounds having a carboxyl group, $-COOH$, linked to the hydrocarbon radical, *i.e.*, $R-COOH$).

By passing the vapour of methanol and air over copper catalyst at about 600°, formaldehyde is manufactured. This has a great demand in the plastics industry and most of the methanol of today is converted into formaldehyde.

Methyl alcohol (as also other alcohols) reacts with metallic sodium and forms sodium methoxide (or alcoholate).

$$\underset{\text{Methyl alcohol}}{2CH_3OH} + 2Na = H_2 + \underset{\text{Sodium methoxide}}{2CH_3ONa.}$$

With conc. H_2SO_4, methanol first gives methyl hydrogen sulphate and then dimethyl sulphate.

$$\underset{\text{Methyl alcohol}}{CH_3OH} + H_2SO_4 = \underset{\text{Methyl hydrogen sulphate}}{CH_3.HSO_4} + H_2O.$$

$$CH_3.HSO_4 + CH_3OH = \underset{\text{Dimethyl sulphate}}{(CH_3)_2SO_4} + H_2O.$$

With excess of H_2SO_4 and on heating, it forms dimethyl ether:

$$\underset{\text{Methyl alcohol}}{2CH_3OH} = \underset{\text{Dimethyl ether}}{CH_3.O.CH_3} + H_2O.$$

Uses.—Methanol is chiefly used for the manufacture of formaldehyde and to some extent, dyestuffs, perfumes, etc. It is employed in making varnishes, as a motor fuel mixed with petrol, in making methylated spirit in many countries but not in India and also as a solvent for lacquer varnish, castor oil, etc.

Methyl alcohol does not yield iodoform like ethyl alcohol. If a piece of red-hot copper gauze be plunged into a test-tube containing a few drops of methyl alcohol, a pungent odour of formaldehyde becomes immediately apparent.

Ethyl alcohol, ethanol, C_2H_5OH, the oldest known alcohol, is simply called 'alcohol'; it is also known as 'spirit of wine' or grain alcohol in commerce. It is usually made by *fermentation* (*fervere,* to boil) of sugar solutions with yeast, a low form of plant life having only one cell. The process of making alcohol from sugar, grape-sugar or glucose, for example, with yeast is a catalytic one, the catalyst is a complex organic compound, *zymase,* secreted by the yeast. A dilute glucose solution is decomposed by yeast at room temperature mainly into alcohol and CO_2.

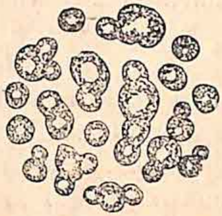


Fig. 26. Yeast cells, highly magnified.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} = \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2.$$

Yeast usually contains another catalyst called *invertase* which splits up cane-sugar into its components, glucose and fructose (or fruit-sugar). These are then attacked by zymase and alcohol is produced as from glucose.

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}.$$

Alcohol is manufactured from cheaper products like rice, oat, potato, maize, or molasses from sugar factories (as in India) but never from cane-sugar.

Rice, maize, potato, etc. chiefly consist of starch, a complex compound, having the molecular formula, $(C_6H_{10}O_5)n$, n is very large but as yet not definitely known. Starch is anhydro-glucose polymerised; so by hydrolysis, we get mainly glucose therefrom. Yeast cells cannot attack such big molecules as starch; they are, therefore, first broken into small units by another organic catalyst or enzyme called *diastase* or *amylase* which occurs in malt or germinating barley.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)n} + nH_2O \xrightarrow{\text{diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}.$$

This simpler sugar is then decomposed by yeast which contains the enzyme, *maltase*, into glucose.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{2C_6H_{12}O_6}.$$

Glucose is finally split up into alcohol and CO_2 by the *zymase* of yeast at about 30° in about four days. The yield of alcohol from starch is nearly 80%. The resulting mixture is distilled to obtain alcohol. Fermentation alcohol is rather dilute—about 50% ; concentrated alcohol kills the yeast cells. By fractional distillation or rectification in Coffey's still, alcohol (b.p. 78·5°) is separated from water (b.p. 100°). We cannot thus get pure or *absolute alcohol,* free from water, for alcohol (95·6%) and water (4·4%) form a constant-boiling mixture which distils like a pure organic liquid at 78·15°. This is called *rectified spirit,* extensively used in medicine. Dehydrating agents like quicklime (but not calcium chloride) take up the residual water from rectified spirit and by a second distillation *absolute alcohol* is obtained. It contains 0·1-1% water. In countries having little petroleum, alcohol is mixed with petrol for motor vehicles. Alcohol employed for the generation of power is called *power alcohol.*

Properties.—Ethyl alcohol is a colourless, volatile, neutral liquid with a pleasant smell and a burning taste. It boils at 78·5°, is lighter than water (sp. gr. 0·789) and mixes with it in all proportions. As it freezes at −114°, it is used in some forms of thermometer for measuring low temperature in place of mercury. It is highly hygroscopic *i.e.,* absorbs moisture from the air. In small doses, alcohol is a good stimulant but it acts as a poison when taken in large quantities. It dissolves many organic compounds and is a useful solvent.

With iodine and alkali, ethyl alcohol gives iodoform—a reaction by which it is often detected and also distinguished from methanol. With sodium acetate and H_2SO_4, it produces the fruity odour of ethyl acetate.

Reactions.—Alcohols are much more reactive than paraffins. The reactions of ethyl alcohol are representative of other primary monohydric alcohols.

(*i*) Metallic sodium or potassium liberates hydrogen, producing the ethoxide or alcoholate at ordinary temperature. This crystallises out readily.

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2Na = H_2 + \underset{\text{Sodium alcoholate}}{2C_2H_5ONa}.$$

(*ii*) Phosphorus tri- or penta-chloride gives ethyl chloride (p. 42).

$$3C_2H_5OH + PCl_3 = H_3PO_3 + \underset{\text{Ethyl chloride}}{3C_2H_5Cl}.$$

$$C_2H_5OH + PCl_5 = C_2H_5Cl + HCl + POCl_3.$$

(*iii*) With acids and in presence of a dehydrating agent such as conc. H_2SO_4, HCl gas, etc. *esters* are formed (p. 44).

$$C_2H_5\boxed{OH + H}Cl = \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O.$$

$$C_2H_5\boxed{OH + H}\underset{\text{Acetic acid}}{OOC.CH_3} = \underset{\text{Ethyl acetate}}{C_2H_5.OOC.CH_3} + H_2O.$$

(*iv*) With conc. H_2SO_4,

(*a*) at about 100°, in equal volumes, ethyl hydrogen sulphate is formed:

$$C_2H_5\boxed{OH + H.}HSO_4 = \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5.HSO_4} + H_2O.$$

(*b*) at about 165° if the *acid* be in excess, ethylene results (p. 34):

$$C_2H_5OH + H_2SO_4 = \underset{\text{Ethylene}}{C_2H_4} + H_2O + H_2SO_4.$$

(*c*) at about 140°, if *alcohol* be in excess, ether is produced, ethyl hydrogen sulphate being an intermediate product:

$$2C_2H_5OH \xrightarrow{-H_2O} \underset{\text{Ether}}{C_2H_5-O-C_2H_5}.$$

✓ (*v*) Oxidising agents *e.g.*, potassium dichromate and H_2SO_4, or air in presence of a catalyst, convert alcohol first into acetaldehyde and then into acetic acid (*cf.* methanol, p. 52). HNO_3 finally gives oxalic acid. HOOC-COOH.

$$\underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \xrightarrow{O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH.}$$

(*vi*) With chlorine, alcohol first forms acetaldehyde and finally, chloral (p. 46). Bromine acts likewise but iodine has no action. Its solution in alcohol is 'tincture of iodine' used in medicine.

$$CH_3CH_2OH + Cl_2 = \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HCl.$$

$$CH_3CHO + 3Cl_2 = \underset{\text{Chloral}}{CCl_3.CHO} + 3HCl.$$

✓ (*vii*) With bleaching powder and water, it gives chloroform (p. 46).

(*viii*) Alcohol reacts with bromine (or iodine) and red phosphorus giving ethyl bromide (or iodide). See p. 43.

✓ (*ix*) With iodine and alkali, it gives iodoform (p. 48).

Uses.—Alcohol is a common drink in the form of beer, whisky, wine, gin, rum, etc. containing varying amounts of it. Mixed with methyl alcohol, it forms methylated spirit, a solvent for lac, lacquer, etc. As power alcohol for motor vehicles, mixed with petrol, it is now used in India. For sterilisation in surgery, in medicine for making various tinctures, in spirit lamps, and also in making some dyes and drugs alcohol has wide application. In India methylated spirit is made by adding pyridine and light caoutchoucine to ethyl alcohol, so it is not 'methylated' at all. The action of alcohol as an antiseptic is believed to be due to its strong dehydrating power—it kills bacteria by dehydration.

Amyl alcohols, $C_5H_{12}O$.—There should be eight isomeric amyl alcohols, all are known. Of these, isobutyl carbinol, $CH_3CH(CH_3).CH_2.CH_2OH$ (b.p. 131°) and active amyl alcohol, $CH_3CH_2CH(CH_3)CH_2OH$, (b.p. 128°) occur in fusel oil which is the last fraction in the distillation of crude spirit made from starch by fermentation.

Amyl alcohols are sparingly soluble in water. Amyl nitrate is used in medicine, and amyl acetate as a solvent for lacquers. Amyl alcohols of fusel oil are industrially important.

Polyhydric alcohols.—The simplest dihydric alcohol *viz.* methylene alcohol, $CH_2(OH)_2$, is unknown. *Two* hydroxyl groups linked to the *same* carbon atom make it extremely unstable. The next member, ethylene glycol, $HOCH_2.CH_2OH$, is commercially important.

Glycol, ethylene glycol, $CH_2OH—CH_2OH$, is made in the laboratory by boiling ethylene dibromide with a dilute solution of potassium carbonate.

$$\underset{\text{Ethylene dibromide}}{BrH_2C.CH_2Br.} + K_2CO_3 + H_2O = \underset{\text{Glycol}}{CH_2OH.CH_2OH} + 2KBr + CO_2.$$

It is manufactured from ethylene by reacting with hypochlorous acid (bleaching powder and CO_2) at about 0°. Ethylene chlorhydrin, thus formed, is hydrolysed with sodium bicarbonate solution to glycol.

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + HOCl = \underset{\text{Ethylene chlorhydrin}}{ClH_2C.CH_2OH.}$$

$$ClH_2C.CH_2OH + NaHCO_3 = \underset{\text{Glycol}}{HOH_2C.CH_2OH} + NaCl + CO_2.$$

Glycol results when ethylene is oxidised with a dilute alkaline solution of $KMnO_4$ (p. 36).

Properties.—Glycol is a sweet (Greek, *glykus,* sweet), colourless, syrupy liquid (b.p. 197°) without any smell. It is much heavier than alcohol (sp. gr. 1·17) and mixes with water in all proportions. As it melts at —11·5°, it is extensively employed as an anti-freeze in motor car radiators in cold countries. A 60% aqueous solution melts at —49°. It is also an industrial solvent.

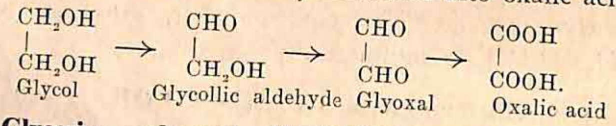
Glycol gives all the reactions of ethyl alcohol, for example, with sodium it forms first a mono- and then a di-sodium derivative:

$$\underset{\text{Glycol}}{HOH_2C.CH_2OH} \longrightarrow \underset{\text{Sodium glycolate}}{NaOH_2C.CH_2OH} \longrightarrow \underset{\text{Disodium glycolate}}{NaOCH_2.CH_2ONa.}$$

With PCl_5, it gives ethylene dichloride:

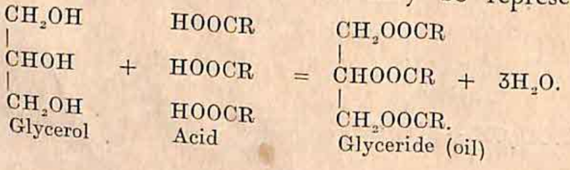
$$\underset{\text{Glycol}}{HOH_2C.CH_2OH} \xrightarrow{PCl_5} \underset{\text{Ethylene dichloride}}{Cl.H_2C.CH_2Cl.}$$

On oxidation, it is finally converted into oxalic acid:



$$\underset{\text{Glycol}}{\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}} \rightarrow \underset{\text{Glycollic aldehyde}}{\begin{array}{c}CHO\\|\\CH_2OH\end{array}} \rightarrow \underset{\text{Glyoxal}}{\begin{array}{c}CHO\\|\\CHO\end{array}} \rightarrow \underset{\text{Oxalic acid}}{\begin{array}{c}COOH\\|\\COOH.\end{array}}$$

Glycerine, glycerol, $HOH_2C.CHOH.CH_2OH$, is the common constituent of all animal and vegetable oils and fats, *e.g.*, cocoanut oil, ghee, mustard oil, lard, olive oil, linseed oil, palm oil, etc. Fats and oils are esters (or organic salts) of glycerol with organic acids such as oleic acid, stearic acid, palmitic acid, etc. They are consequently known as *glycerides*. Formation of oils may be represented as



$$\underset{\text{Glycerol}}{\begin{array}{c}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}} + \underset{\text{Acid}}{\begin{array}{c}HOOCR\\ \\HOOCR\\ \\HOOCR\end{array}} = \underset{\text{Glyceride (oil)}}{\begin{array}{c}CH_2OOCR\\|\\CHOOCR\\|\\CH_2OOCR.\end{array}} + 3H_2O.$$

Hence, glycerol results when fats and oils are hydrolysed, for example, with caustic soda. Sodium salts of these fatty acids (so named because they occur in fats and oils) are the soaps of our daily use. Glycerol is a bye-product in the manufacture of soap.

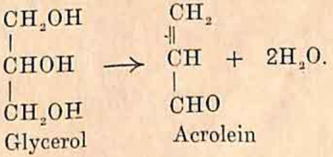
$$\text{Oils} + NaOH = \underset{\text{(soap)}}{\text{sodium salts of fatty acids}} + \text{glycerol.}$$

The soap lye, after the separation of soap, contains 5-8% glycerol. The liquid is filtered. Glycerol is concentrated under reduced pressure. It is purified by distillation under reduced pressure but in a current of steam. The water is finally removed by evaporation under reduced pressure.

Glycerine is a bye-product in alcoholic fermentation, about 3% is formed with alcohol. But if fermentation is carried out in presence of much sodium sulphite, the yield of glycerol goes up to 36%. Glycerine from molasses was thus commercially made for explosives by Germany during the first world war when she was short of fats.

Properties.—Glycerine is a colourless, odourless, syrupy liquid (sp. gr. 1·265), miscible with water in all proportions. It is very hygroscopic. Glycerine boils at 290° with slight decomposition. It is sweet to the taste and is an antiseptic.

Glycerol reacts with sodium liberating hydrogen ; with PCl_5, all the three —OH groups are replaced by Cl, glycerine trichloride, $ClH_2C-CHCl-CH_2Cl$, being formed. Dehydrating agents such as P_2O_5 or $KHSO_4$, produce acrolein which has a pungent odour. Acrolein is also formed when oils and fats are over-heated.



$$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CHO \end{matrix} + 2H_2O.$$

Glycerol Acrolein

Uses.—By far the largest quantity of glycerol is used in making nitro-glycerine, an explosive. *Dynamite* is a mixture of 75% nitro-glycerine in kieselguhr; it was discovered by Alfred Nobel of Sweden, who inaugurated the Nobel Prizes. Blasting gelatine, cordite, etc. also contain nitro-glycerine. Glycerol is employed in the manufacture of cosmetics, cigarettes, type-writer ribbons; in medicine, as an anti-freeze, and in making plastics.

Questions

1. Describe carefully the manufacture of ethyl alcohol. How will you prove its structure? I.Sc. 1950, Nagpur Uni.

2. What is glycerol? To what class of compounds does it belong? Give one method of preparation of this substance in pure state and on a large scale. State the different preparations in which glycerol is used. I.Sc. 1950, Nagpur University.

3. What are primary, secondary and tertiary monohydric alcohols? How are they distinguished from one another? How can methyl alcohol be converted into ethyl alcohol?

I.Sc. 1951, Nagpur University.

4. What are glycols? Give the method of preparation and properties of ethylene glycol and state its oxidation products.

I.Sc. 1953, Nagpur Uni.

5. What is alcoholic fermentation? How is it used in making ethyl alcohol from starch? How will you distinguish ethyl alcohol from methyl alcohol? I.Sc. Sup. 1953, Nagpur Uni.

6. What is pyroligneous acid and how is it obtained? What simple compounds does it contain and how are they separated?

I.Sc. 1954, Patna Uni.

7. How are the following obtained from potatoes? Rectified spirit, methylated spirit and absolute alcohol. What are the important uses of ethyl alcohol? I.Sc. 1952, E. Punjab Uni.

CHAPTER VIII

Ethers.—If from two molecules of a monohydric alcohol, one molecule of water be eliminated, we get an *ether*:

$$\underset{\text{Alcohol}}{\mathrm{RO}\boxed{\mathrm{H + HO}}\mathrm{R}} = \underset{\text{Ether}}{\mathrm{R{-}O{-}R}} + \mathrm{H_2O},$$

R representing an alkyl group. Ethers are also termed *alkyl oxides,* R_2O. They may be regarded as derivatives of water, both the hydrogen atoms of which have been replaced by alkyl radicals:

$$\underset{\text{Water}}{\mathrm{H{-}O{-}H}}, \qquad \underset{\text{Alcohol}}{\mathrm{H{-}O{-}R}}, \qquad \underset{\text{Ether}}{\mathrm{R{-}O{-}R}}$$

The general formula for ethers is $C_nH_{2n+2}O$, the same as for alcohols, *viz.* $C_nH_{2n+1}OH$. Ethers are, therefore, isomeric with alcohols. In properties, however, they are quite different from alcohols. Common ether is diethyl ether, $C_2H_5OC_2H_5$.

The first member of the series, dimethyl ether, $CH_3.O.CH_3$, is isomeric with ethyl alcohol. The next one, the most important, is diethyl ether, $C_2H_5.O.C_2H_5$, (isomeric with butyl alcohol); it is simply called ether. If the two alkyl groups attached to oxygen are the same, as in dimethyl and diethyl ether, we get *simple ethers*; if different as in methyl ethyl ether, $CH_3.O.C_2H_5$, we have *mixed* ethers.

Diethyl ether, $C_2H_5.O.C_2H_5$, is prepared, both in the laboratory and in industry, by heating an *excess* of ethyl alcohol with conc. H_2SO_4 at 130°—140°. The acid eliminates a mol. of water from *two* molecules of the alcohol. The reaction takes place in two stages:

$$(i)\quad \underset{\text{Alcohol}}{\mathrm{C_2H_5OH}} + \mathrm{H_2SO_4} \Longleftrightarrow \underset{\text{Ethyl hydrogen sulphate}}{\mathrm{C_2H_5H.SO_4}} + \mathrm{H_2O}.$$

$$(ii)\quad \mathrm{C_2H_5}\boxed{\mathrm{HSO_4 + H}}\mathrm{O.C_2H_5} = \underset{\text{Ether}}{\mathrm{C_2H_5.O.C_2H_5}} + \mathrm{H_2SO_4}.$$

Ethanol with excess of conc. H_2SO_4 gives ethylene at about 160° (p. 34), dehydration being within the molecule.

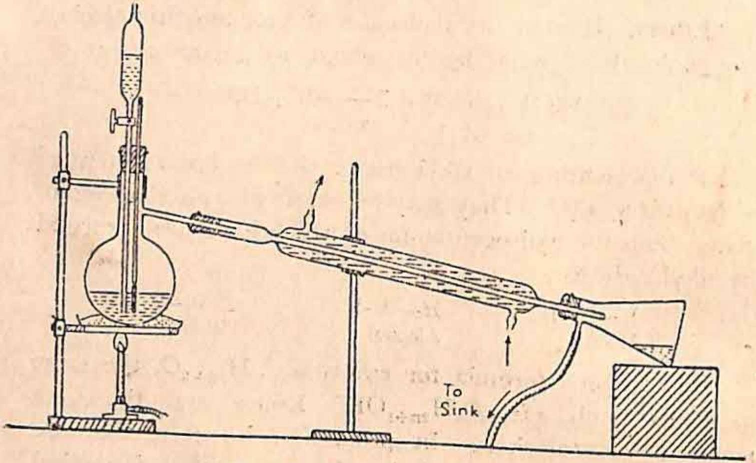


Fig. 27. Preparation of ether.

The sulphuric acid, regenerated in the second stage, converts fresh alcohol into ether; this may go on. Hence the process is called *continuous etherification process*. In actual practice, however, the process is not continuous due to side-reactions, etc. Rectified spirit, mixed carefully with an equal volume of conc. H_2SO_4, is taken in the flask which is heated on a sand-bath to 140°—145°. Ice-cold water is circulated through the condenser the end of which leads to a receiver. To avoid fire hazard (ether is very highly inflammable), the side-tube of the receiver is connected by a rubber tube to the sink. Fresh alcohol is added from the tap-funnel to keep the volume in the flask constant. The ether is washed with water, dehydrated with calcium chloride and re-distilled.

(2) By heating sodium alcoholate with ethyl iodide in alcoholic solution under reflux, ether is obtained:

$$\underset{\text{Sodium alcoholate}}{C_2H_5O}\boxed{Na + I}C_2H_5 = \underset{\text{Ether}}{C_2H_5.O.C_2H_5} + NaI.$$

By using methyl or butyl iodide, a mixed ether may be obtained. This elegant synthesis was discovered by Williamson in 1852. The constitution of ethers follows from this synthesis because the reaction cannot take a different course.

By reacting conc. H_2SO_4 with a mixture of methanol and ethanol, we get methyl ethyl ether, $CH_3.O.C_2H_5$, besides dimethyl ether and diethyl ether.

Properties.—Ether is a colourless, neutral, highly volatile liquid (b.p. 34·5°) with a characteristic smell and a burning taste. The vapour forms an explosive mixture with air. It is much lighter than water (sp. gr. 0·72) and is only slightly soluble in it. By rapid evaporation, it produces intense local cooling and so is used as a local anæsthetic. Unlike alcohol, ether is chemically inert, metals like sodium and potassium have no action on it. These react with the —OH group of alcohols, which is absent in ethers.

With PCl_5, ether forms ethyl chloride on heating.

$$\underset{\text{Ether}}{C_2H_5.O.C_2H_5} + PCl_5 = \underset{\text{Ethyl chloride}}{2C_2H_5Cl} + POCl_3.$$

Hydriodic acid gas at 0° decomposes ether into ethyl iodide and alcohol:

$$\underset{\text{Ether}}{C_2H_5.O.C_2H_5} + HI = \underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}.$$

But hot and conc. HI produces only ethyl iodide:

$$\underset{\text{Ether}}{C_2H_5.O.C_2H_5} + 2HI = \underset{\text{Ethyl iodide}}{2C_2H_5I} + H_2O.$$

Heated under pressure with dilute H_2SO_4, ether is hydrolysed to alcohol:

$$\underset{\text{Ether}}{C_2H_5.O.C_2H_5} + H_2O = \underset{\text{Alcohol}}{2C_2H_5OH}.$$

Diethyl ether is in no way related to the hypothetical 'ether' of the physicist, or the so-called fifth element of the Hindus, and should be confused with neither.

Uses.—Ether is widely used as an anæsthetic with chloroform in surgical operations. It is a common solvent for resins, fats, nitrocellulose and many other organic compounds. Mixed with alcohol, it forms a petrol substitute.

Dimethyl ether, $CH_3O.CH_3$, is prepared by heating methyl alcohol with conc. H_2SO_4 in the same way as diethyl ether, or by heating methyl iodide with sodium methoxide in methyl alcoholic solution. It is a colourless gas which can be condensed to a liquid (b.p. —23°). Dimethyl ether is sometimes used for producing artificial cold.

A re-arrangement of the alkyl groups on either side of the oxygen atom gives rise to isomeric ethers. Thus $C_4H_{10}O$ is diethyl ether, $C_2H_5.O.C_2H_5$, or methyl propyl ether, $CH_3.O.C_3H_7$. This isomerism amongst compounds of the same class is called *metamerism.*

Questions

1. Write the names and structural formulæ for two compounds represented by the molecular formula C_2H_6O. By what characteristic reactions can they be identified? What kind of relationship exists in such class of substances? I.Sc. 1950, Nagpur University.

2. What compounds would be represented by the molecular formula $C_4H_{10}O$? State reactions by which one can be distinguished from the other. I.Sc. 1955, Nagpur Uni.

3. How is ether prepared in the laboratory? Mention its important properties. What are its uses?

4. Write short notes on : continuous etherification process, Williamson's synthesis, simple and mixed ethers, metamerism.

5. What substances can you prepare from ethyl alcohol and H_2SO_4?

CHAPTER IX

Aldehydes and ketones.—A primary alcohol, on mild oxidation, parts with two atoms of hydrogen and passes on to an **aldehyde.** The term aldehyde means alcohol deprived of hydrogen (*al*cohol *dehyd*rogenatum). Aldehydes have the general formula R-CHO.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{-2H} \underset{\text{Acetaldehyde}}{CH_3CHO.}$$

The monovalent aldehyde group, —CHO, is typical of aldehydes as —CH_2OH of primary alcohols. We can recognise an aldehyde from its structural formula.

A secondary alcohol, on oxidation, yields a **ketone.**

$$\underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3} \xrightarrow{-2H} \underset{\text{Dimethyl ketone}}{CH_3.CO.CH_3.}$$

The bivalent carbonyl or ketone group, $>C=O$, is common to all ketones. Since the aldehyde group is graphically represented as $\overset{H}{}\!\!>C=O$, it may be noted that the $>C=O$ group is common to both aldehydes and ketones. Consequently, many of their reactions are similar. The structural difference between an aldehyde and a ketone is that in the case of aldehyde, one valency of the carbonyl carbon is satisfied by hydrogen while in ketones *both* the valency bonds are linked with hydrocarbon radicals.

Since both aldehydes and ketones are derived from monohydric alcohols, $C_nH_{2n+1}OH$, primary or secondary, by the removal of two hydrogen atoms, their general formula is the same *viz.*, $C_nH_{2n}O$. Aldehydes are, therefore, isomeric with ketones.

$$\underset{C_3H_8O\text{, normal propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{-2H} \underset{\text{Propionaldehyde, } C_3H_6O.}{CH_3CH_2CHO.}$$

$$\underset{C_3H_8O,\ \text{isopropyl alcohol}}{CH_3CHOHCH_3} \xrightarrow{-2H} \underset{\text{Dimethyl ketone, } C_3H_6O.}{CH_3COCH_3.}$$

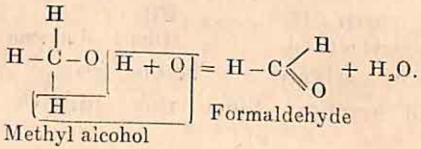
Formaldehyde, $HCHO$, and acetaldehyde, CH_3CHO, are the most important. Aldehydes are commonly named after the acids they yield on further oxidation:

$$\underset{\text{Methyl alcohol}}{HCH_2OH} \longrightarrow \underset{\text{Formaldehyde}}{HCHO} \longrightarrow \underset{\text{Formic acid}}{HCOOH}$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}$$

They are also named by substituting '-al' for '-e' in paraffins, *e.g.*, methanal, HCHO.

Formaldehyde, HCHO, is prepared by passing a mixture of air and methyl alcohol vapour over copper gauze at about 600°.



$$\underset{\text{Methyl alcohol}}{H-\overset{H}{\underset{H}{C}}-O\,\boxed{H + O}} = \underset{\text{Formaldehyde}}{H-C\begin{matrix}\diagup H\\ \diagdown\!\!\diagdown O\end{matrix}} + H_2O.$$

The out-going vapour is absorbed in water, 30 40% formaldehyde is thus obtained.

Properties.—Formaldehyde is a colourless gas with a very pungent smell. It can be condensed to a liquid (b.p. −21°). The gas is highly soluble in water, a 40% solution, called *formalin,* is sold in the market. Formaldehyde readily coagulates proteins—it is believed that the aldehyde kills bacteria similarly. It is a good antiseptic.

Formaldehyde is readily oxidised to formic acid, $HCOOH$, and reduced to methyl alcohol, CH_3OH. The reactions of formaldehyde are more or less similar to those of acetaldehyde, which are described later.

Uses.—Formaldehyde is mainly employed for the manufacture of synthetic resins or plastics such as bakelite, galalith, etc., made respectively from phenol and formaldehyde, and casein (of milk) and formaldehyde. It is also used as an antiseptic and a disinfectant, in making some dyes and drugs, as well as in the preservation of anatomical and biological specimens.

✓**Acetaldehyde, CH_3CHO.**—In the laboratory, it is prepared by oxidising ethyl alcohol with sodium dichromate and H_2SO_4. The mixture is distilled from a flask heated on a sand-bath; ice-cold water is circulated through the condenser, the end of which leads through an adaptor to a receiver cooled in ice. The aldehyde distils off continuously from the reaction vessel and thus escapes further oxidation to acetic acid.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + O = \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O.$$

Acetaldehyde is manufactured from acetylene, C_2H_2, which combines with water in presence of mercuric sulphate at about 100° (p. 40).

$$\underset{\text{Acetylene}}{HC \equiv CH} + H_2O = \underset{\text{Acetaldehyde}}{CH_3CHO}.$$

Properties.—Acetaldehyde is a colourless, mobile liquid (b.p. 21°) with a pungent smell. It mixes with water, alcohol, benzene and ether in all proportions. It is lighter than water (sp. gr. 0·80).

Reactions.—(*i*) On oxidation *e.g.*, with potassium dichromate and H_2SO_4, acetaldehyde gives acetic acid which contains the *same* number of carbon atoms as the aldehyde:

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + O = \underset{\text{Acetic acid}}{CH_3COOH}.$$

(*ii*) On reduction, *e.g.*, with sodium amalgam and water, acetaldehyde passes back to ethyl alcohol:

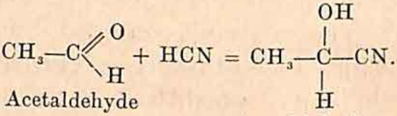
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2H = \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}.$$

(*iii*) With a cold, *saturated* solution of sodium bisulphite, acetaldehyde yields a crystalline bisulphite compound:

$$CH_3CHO + NaHSO_3 = \underset{\text{Bisulphite compound}}{CH_3CH(OH).SO_3Na.}$$

The aldehyde can be obtained back by heating this compound with dilute acids; this is useful for the purification of aldehydes.

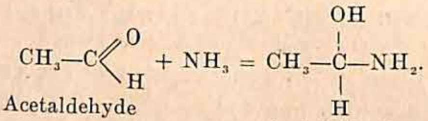
(*iv*) With hydrocyanic acid, acetaldehyde forms *cyanhydrin:*



Acetaldehyde

Acetaldehyde cyanhydrin

(*v*) With dry ammonia, it forms *aldehyde-ammonia* which is crystalline, soluble in water but insoluble in ether:



Acetaldehyde

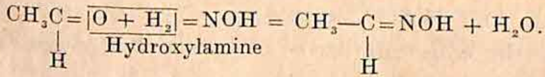
Acetaldehyde-ammonia

With ammonia, formaldehyde forms no addition product but gives hexamine, $(CH_2)_6N_4$, a condensation product, used in medicine.

(*vi*) Acetaldehyde reacts with PCl_5 and forms ethylidene chloride:

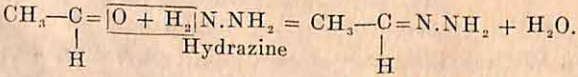
$$CH_3CHO + PCl_5 = \underset{\text{Ethylidene chloride}}{CH_3CHCl_2} + POCl_3.$$

(*vii*) With hydroxylamine, it gives an *aldoxime:*

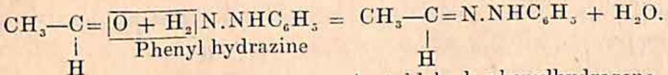


$$\underset{\substack{|\\H}}{CH_3C}=\underset{\text{Hydroxylamine}}{\overline{|O + H_2|}=NOH} = \underset{\text{Acetaldoxime}}{CH_3-\underset{\substack{|\\H}}{C}=NOH} + H_2O.$$

(*viii*) Acetaldehyde combines with hydrazine or phenylhydrazine to form a *hydrazone* or a *phenylhydrazone*, which are crystalline compounds:



$$CH_3-\underset{\substack{|\\H}}{C}=\underset{\text{Hydrazine}}{\overline{|O + H_2|}N.NH_2} = \underset{\text{Acetaldehyde hydrazone}}{CH_3-\underset{\substack{|\\H}}{C}=N.NH_2} + H_2O.$$



$$CH_3{-}\underset{\underset{H}{|}}{C}=\boxed{O + H_2}N.NHC_6H_5 = CH_3{-}\underset{\underset{H}{|}}{C}=N.NHC_6H_5 + H_2O.$$

Phenyl hydrazine

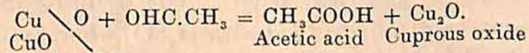
Acetaldehyde phenylhydrazone

(*ix*) Acetaldehyde, like other aldehydes, is a strong reducing agent, on account of the readiness with which it gets oxidised.

(*a*) Ammoniacal solution of silver nitrate is reduced to metallic silver on warming with acetaldehyde; a mirror of silver is thus produced.

$$Ag_2O + CH_3CHO = \underset{\text{Acetic acid}}{CH_3COOH} + 2Ag.$$

(*b*) Red oxide of copper separates on warming acetaldehyde with Fehling's solution:



$$\begin{matrix}Cu\\CuO\end{matrix}\searrow O + OHC.CH_3 = \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Cuprous oxide}}{Cu_2O}.$$

Cupric oxide

(*c*) Acetaldehyde restores the colour of Schiff's reagent (magenta solution made colourless with SO_2) in the cold.

Polymerisation.—Aldehydes polymerise readily *i.e.*, two or more molecules combine together to form a new, more complex compound, the mol. wt. of which is a multiple of that of the original compound. Anhydrous acetaldehyde forms *paraldehyde*, $(CH_3CHO)_3$, when a little conc. H_2SO_4 is added to it. It is a colourless liquid (b.p. 124°) with a pleasant odour, but sparingly soluble in water. It is a hypnotic, *i.e.*, produces sleep.

With dilute H_2SO_4 or $CaCl_2$ at low temperature, acetaldehyde forms *metaldehyde*, $(CH_3CHO)_n$, which is a crystalline solid, n being not known definitely.

With potassium carbonate or $ZnCl_2$, acetaldehyde gives a third polymer, *aldol*, $CH_3CH(OH)CH_2CHO$.

Similarly, formaldehyde polymerises under suitable conditions into solid *paraform* or *paraformaldehyde,* $(HCHO)_n$ and *metaformaldehyde,* $(HCHO)_3$.

Formaldehyde is believed to be the basic compound that polymerises to sugars (such as glucose) which are ultimately converted by nature into complex bodies like starch or cellulose. CO_2 of the air possibly combines with water of plants in presence of light and chlorophyll to form formaldehyde.

$$CO_2 + H_2O \longrightarrow \underset{\text{Formaldehyde}}{HCHO} \longrightarrow \underset{\text{Sugars}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n}$$

Acetaldehyde is used in dye manufacture, paraldehyde in medicine and metaldehyde as a solid fuel for spirit lamps.

Chloral, CCl_3CHO, is made by passing chlorine into alcohol, first at 20° and then at 90°. The resulting product, a solid, is separated and distilled with H_2SO_4 whereby chloral is obtained. The reaction is complex, chlorination and oxidation taking place simultaneously.

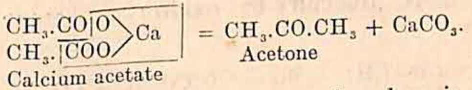
With water, it gives a hydrate, called chloral hydrate, CCl_3CHO,H_2O, or $CCl_3CH(OH)_2$, which is a hypnotic in medicine. D. D. T. is made from chloral.

Ketones.—As already mentioned, ketones are compounds containing a carbonyl group, $>CO$, linked to two hydrocarbon radicals. Their general formula, therefore, is R_1-CO-R_2, R_1 and R_2 may be the same or different, giving *simple* or *mixed* ketones (*cf.* simple and mixed ethers, p. 61). Ketones are usually named according to the alkyl groups they contain.

$$\underset{\text{Acetone (simple ketone)}}{CH_3—CO—CH_3} \qquad \underset{\text{Methyl ethyl ketone (mixed ketone)}}{CH_3—CO—C_2H_5}$$

Acetone, dimethyl ketone, CH_3COCH_3, is the simplest and also the most important member of the series. It occurs in traces in blood and urine; it is one of the products of the destructive distillation of wood (p. 51).

Preparation.—(*i*) In the laboratory as also on the commercial scale, acetone is made by the dry distillation of fused calcium acetate (gray acetate of lime of the wood distillation industry).



$$\underset{\text{Calcium acetate}}{\left.\begin{array}{l}CH_3.CO\overline{|O}\\ CH_3.\overline{|COO}\end{array}\right\rangle Ca} = \underset{\text{Acetone}}{CH_3.CO.CH_3} + CaCO_3.$$

Fused and powdered calcium acetate is taken in the retort which is heated on a wire gauze. Acetone distils over and is collected in the receiver (Fig. 28).

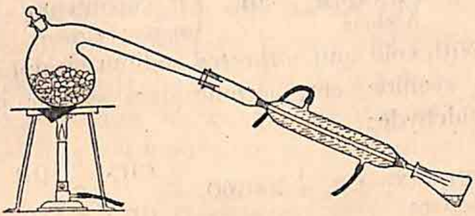


Fig. 28. Preparation of acetone.

(*ii*) Acetone is also manufactured by passing vapour of acetic acid over alumina, Al_2O_3, or thoria, ThO_2, at about 400°. The yield is quite high.

$$\underset{\text{Acetic acid}}{CH_3CO\overline{|OH + H|}\ \overline{\underline{|OOC|}}CH_3} = \underset{\text{Acetone}}{CH_3.CO.CH_3} + CO_2 + H_2O.$$

(*iii*) By passing ethyl alcohol and steam over catalysts, Great Britain makes acetone:

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + H_2O = \underset{\text{Acetone}}{CH_3COCH_3} + 4H_2 + CO_2.$$

Isopropyl alcohol yields acetone on oxidation; by fermentation of starchy materials with *Fernbach's bacillus*, in absence of air, acetone may be obtained in good yield.

Properties.—Acetone is a colourless liquid (b.p. 56·5°) with a pleasant smell and a burning taste. It mixes with water in all proportions and is lighter (sp. gr. 0·792). It dissolves good many organic compounds and is consequently a valuable solvent.

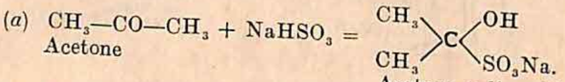
Reactions.—(*i*) On oxidation, acetone yields acetic acid (with a *lesser* number of carbon atoms) and CO_2. It is generally more difficult to oxidise a ketone than an aldehyde.

$$\underset{\text{Acetone}}{CH_3{-}CO{-}CH_3} + 4O = \underset{\text{Acetic acid}}{CH_3COOH} + CO_2 + H_2O.$$

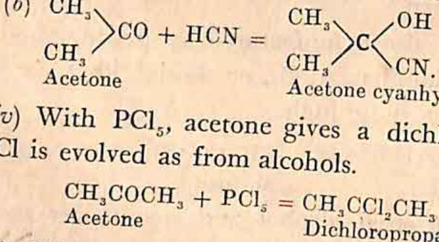
(*ii*) On reduction *e.g.*, with sodium amalgam, it gives back isopropyl alcohol:

$$\underset{\text{Acetone}}{CH_3COCH_3} + 2H = \underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3}.$$

(*iii*) With cold and *saturated* sodium bisulphite solution, potassium cyanide, etc., acetone gives similar products as does acetaldehyde:



$$(a)\quad \underset{\text{Acetone}}{CH_3{-}CO{-}CH_3} + NaHSO_3 = \underset{\text{Acetone sodium bisulphite}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}OH\\SO_3Na.\end{matrix}}$$



$$(b)\quad \underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO} + HCN = \underset{\text{Acetone cyanhydrin}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}OH\\CN.\end{matrix}}$$

(*iv*) With PCl_5, acetone gives a dichloro-derivative but no HCl is evolved as from alcohols.

$$\underset{\text{Acetone}}{CH_3COCH_3} + PCl_5 = \underset{\text{Dichloropropane}}{CH_3CCl_2CH_3} + POCl_3.$$

(*v*) With hydrazine, phenylhydrazine and hydroxylamine, acetone reacts in the same way as does acetaldehyde and gives similar products:

$$(a)\quad \underset{\text{Acetone}}{(CH_3)_2C}\boxed{O + \underset{\text{Hydrazine}}{H_2}}N.NH_2 = \underset{\text{Acetone hydrazone}}{(CH_3)_2C{=}N.NH_2} + H_2O.$$

$$(b)\quad \underset{\text{Acetone}}{(CH_3)_2C}\boxed{O + \underset{\text{Phenylhydrazine}}{H_2}}N.NHC_6H_5 = \underset{\text{Acetone phenylhydrazone}}{(CH_3)_2C{=}N.NH.C_6H_5} + H_2O.$$

$$(c)\quad \underset{\text{Acetone}}{(CH_3)_2C}\boxed{O + \underset{\text{Hydroxylamine}}{H_2}}N.NOH = \underset{\text{Acetoxime}}{(CH_3)_2C{=}N.NOH} + H_2O.$$

(*vi*) Acetone differs from acetaldehyde in that it does not reduce ammoniacal solution of silver nitrate or Fehling's solution, it shows no tendency to polymerise unlike acetaldehyde. It is reduced to a secondary alcohol, *viz.*, isopropyl alcohol, but acetaldehyde is reduced to a primary alcohol, *viz.*, ethyl alcohol. Acetone is not easily oxidised like acetaldehyde. Unlike acetaldehyde, it gives no ammonia compound also. While on oxidation acetaldehyde forms an acid (*viz.*, acetic acid) with the *same* number of C atoms, acetone gives acids with a *lesser* number of C atoms.

Acetone forms iodoform with iodine and alkali (p. 48) and chloroform with bleaching powder and water (p. 46).

Uses.—Acetone is mainly used as a solvent for nitrocellulose and celluloid, in the manufacture of chloroform, iodoform, cordite, and for storing acetylene (p. 39). ✓

Questions

1. What is acetone? How is it prepared? Compare and contrast the properties of acetone with those of acetaldehyde.

I.Sc. 1951, Nagpur University.

2. Describe the preparation of aectaldehyde and acetone from acetic acid. Compare the chemical properties of acetaldehyde and acetone.

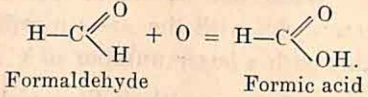
I.Sc. 1953, Bombay Uni.

3. Write a short note on : Polymerisation of formaldehyde and acetaldehyde.

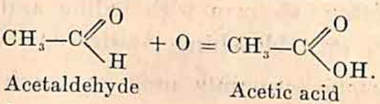
4. How can you obtain (a) acetaldehyde from calcium carbide, (b) acetone from ethyl alcohol, (c) hexamine from methyl alcohol, (d) chloral from ethanol?

CHAPTER X

Aliphatic mono-basic acids.—We have seen that aldehydes take up an atom of oxygen and pass on to acids, the aldehyde group, $-CHO$, being thus converted into a carboxyl group, $-COOH$. Formaldehyde and acetaldehyde yield formic and acetic acid respectively. Acids may be regarded as the final oxidation products of paraffins.



$$\underset{\text{Formaldehyde}}{\mathrm{H{-}C}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\backslash\mathrm{H}}} + \mathrm{O} = \underset{\text{Formic acid}}{\mathrm{H{-}C}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\backslash\mathrm{OH}}}.$$



$$\underset{\text{Acetaldehyde}}{\mathrm{CH_3{-}C}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\backslash\mathrm{H}}} + \mathrm{O} = \underset{\text{Acetic acid}}{\mathrm{CH_3{-}C}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\backslash\mathrm{OH}}}.$$

$$\text{Paraffin} \xrightarrow{\mathrm{O}} \text{Alcohol} \xrightarrow{\mathrm{O}} \text{Aldehyde} \xrightarrow{\mathrm{O}} \text{Fatty acid}$$

$$\underset{\text{Methane}}{CH_4} \longrightarrow \underset{\text{Methyl alcohol}}{CH_3OH} \longrightarrow \underset{\text{Formaldehyde}}{HCHO} \longrightarrow \underset{\text{Formic acid}}{HCOOH}$$

$$\underset{\text{Ethane}}{CH_3.CH_3} \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}.$$

The general formula for the acids of this series may, therefore, be expressed as $R-COOH$. The carboxyl (*carb*onyl, $>CO$, and hydr*oxyl,* $-OH$) radical, $-COOH$, is the characteristic group of organic acids except a few such as HCN, etc. Acids with one $-COOH$ group per molecule are monobasic, with two, dibasic; with three, tribasic and so on; each $-COOH$ group has an ionisable hydrogen, replaceable by metals.

These are commonly known as *fatty acids* because of the fact that acids present in vegetable and animal fats and oils as glycerides, belong to this class, and many of these acids resemble fats physically. Many derive their names from their source, *e.g.*, formic acid from *formica,* ant; acetic acid from *acetum,* vinegar; butyric acid from *butyrum,* butter; capric acid from *capra,* goat, and so on. Their names end in '-ic' while the names of paraffins end in '-ane'. We shall take up the first two members of the series *viz.*, formic and acetic acid.

Formic acid, HCOOH, occurs in red ants and in the stings of bees and wasps which inject a little of it during stinging. It is also present in stinging nettle.

Preparation.—(*i*) Formic acid may be obtained by the oxidation of methyl alcohol or formaldehyde with air in presence of platinum black:

$$\underset{\text{Methyl alcohol}}{CH_3OH} + O = \underset{\text{Formaldehyde}}{HCHO} + H_2O.$$

$$\underset{\text{Formaldehyde}}{HCHO} + O = \underset{\text{Formic acid}}{HCOOH}.$$

(*ii*) In the laboratory, it is usually prepared by heating equal weights of oxalic acid and glycerol (which acts like a catalyst) to about 110°. Heated alone, oxalic acid splits up into formic acid and CO_2 but the yield is poor due to side-reactions. In presence of glycerine, the change is apparently the same but the yield much higher. In its simplest form the reaction is:

$$\underset{\text{Oxalic acid}}{HOOC.COOH} = \underset{\text{Formic acid}}{HCOOH} + CO_2.$$

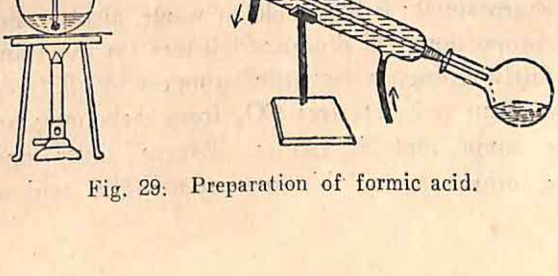


Fig. 29: Preparation of formic acid.

Oxalic acid crystals and glycerine are heated in the flask on a wire-gauze, the bulb of the thermometer dips into the liquid. More oxalic acid is added when the action ceases; formic acid collects with water in the receiver. It is purified by forming lead formate with lead carbonate and decomposing the lead salt with H_2S.

(*iii*) Industrially, formic acid is made by passing carbon monoxide (as producer gas) under pressure over caustic soda at about 210°. Sodium formate is thus obtained:

$$CO + NaOH = \underset{\text{Sodium formate}}{HCOONa}.$$

With cold, *dilute* H_2SO_4, free formic acid is liberated from sodium formate:

$$HCOONa + H_2SO_4 = HCOOH + NaHSO_4.$$

Conc. H_2SO_4 decomposes the formate into carbon monoxide.

$$2HCOONa + H_2SO_4 = 2H_2O + 2CO + Na_2SO_4.$$

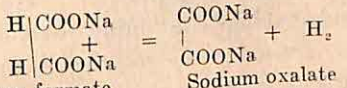
Anhydrous formic acid, therefore, cannot be obtained by reacting a dry formate with conc. H_2SO_4. The acid (b.p. 100·5°) forms a constant-boiling mixture (like ethyl alcohol) with water, which distils like a pure liquid at 107°. Hence by fractional distillation separation from water is not possible. The anhydrous acid is prepared by passing H_2S gas over dry lead formate at 110°; vapour of formic acid passes out (solid lead sulphide is left behind) and gets condensed.

Properties.—Formic acid is a colourless, mobile liquid with a sharp smell; it is soluble in water, alcohol and ether in any proportion. It produces blisters on the skin. The acid is fairly strong, in fact, the strongest of all fatty acids. It turns litmus red, sets free CO_2 from carbonates and also dissolves some metallic oxides. Except silver and lead formates, others are soluble in water. The acid and its salts are readily decomposed by conc. H_2SO_4 into CO. Pure carbon monoxide is made thus.

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O.$$

Unlike other fatty acids, formic acid and formates are reducing agents, behaving more or less like aldehydes in liberating metallic silver from ammoniacal solution of silver nitrate. They also reduce mercuric chloride to mercurous chloride but not Fehling's solution. This is not due to the presence of an aldehyde group as was so long believed. A soluble formate with $AgNO_3$ gives silver formate which, on heating, forms silver. Similarly formed mercuric formate decomposes spontaneously to mercurous formate which gives mercurous chloride with a soluble chloride.

Alkali formates yield alkali oxalates and hydrogen on heating to about 400°. Oxalic acid is now manufactured by this process.



$$\begin{array}{l|l} H & COONa \\ & \quad + \\ H & COONa \end{array} = \begin{array}{l} COONa \\ \mid \\ COONa \end{array} + H_2$$

Sodium formate Sodium oxalate

Uses.—Formic acid is used in coagulating rubber from latex, in tanning for removing lime and also in dyeing wool and cotton. Nickel formate is a catalyst in hydrogenating oils to *Vanaspati*.

Acetic acid, CH_3COOH, is present in sour wine ; vinegar is dilute acetic acid. Croton oil contains the glyceride of acetic acid.

✓ **Preparation.**—(*i*) Ethyl alcohol, on oxidation with potassium dichromate and H_2SO_4, or with oxygen of air in presence of platinum black, yields acetic acid. Great Britain makes acetic acid from denatured alcohol.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH.}$$

(*ii*) Acetylene combines with water in presence of hot, dilute H_2SO_4 and mercuric sulphate, forming acetaldehyde which is then oxidised by air catalytically to acetic acid:

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow{H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH}.$$

Almost pure acetic acid, in high yield, is thus obtained.

(*iii*) Pyroligneous acid (p. 51) of wood distillation, which is made into 'gray acetate of lime' is also a commercial source of the acid. Distilled with H_2SO_4, the gray acetate yields acetic acid:

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + H_2SO_4 = CaSO_4 + \underset{\text{Acetic acid}}{2CH_3COOH}.$$

(*iv*) Dilute acetic acid, in the form of 'vinegar', is made by fermenting *dilute* ethyl alcohol with *Mycoderma aceti,* a living organism, in presence of air. It is a case of oxidation; but the bacteria die in liquids containing more than 15% alcohol. Wood shavings containing the culture of the bacteria are taken in a wooden vessel; the alcohol is run down the shavings while a current of air goes up; the temperature is kept at about 37°. Vinegar thus made contains 4-8% of acetic acid. By repeating the process, the concentration may be raised to about 14%. Usually wine is thus converted into vinegar; pure, dilute alcohol forms no vinegar as it supplies no food for the bacteria.

Properties.—Acetic acid is a colourless liquid (b.p. 118°) with a pungent smell. At about 16°, it forms an ice-like crystalline solid, called *glacial* acetic acid. The acid is miscible with water, alcohol, and ether in all proportions. It is slightly heavier than water (sp. gr. 1·005) and is corrosive. Acetates are soluble in water. With PCl_5 acetic acid forms acetyl chloride, the $-OH$ group is replaced by chlorine. The CH_3CO- group is called *acetyl group.*

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 = \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl.$$

With alcohol and conc. H_2SO_4, it forms ethyl acetate, a sweet-smelling liquid. It is an *ester*.

$$\underset{\text{Acetic acid}}{CH_3COO}|\overline{H + HO}|\underset{\text{Ethyl alcohol}}{C_2H_5} = \underset{\text{Ethyl acetate}}{CH_3COO.C_2H_5} + H_2O.$$

With Cl_2, boiling acetic acid forms mono-, di- and finally tri-chloroacetic acid:

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Cl_2} \underset{\text{Mono-chloro-acetic acid}}{CH_2ClCOOH} \xrightarrow{Cl_2} \underset{\text{Dichloro-acetic acid}}{CHCl_2COOH} \xrightarrow{Cl_2} \underset{\text{Trichloro-acetic acid}}{CCl_3COOH}.$$

Uses.—Acetates of aluminium and chromium are used in dyeing; basic copper acetate makes the pigment *verdigris*. Cellulose acetate forms acetate rayon or artificial silk. Acetic acid is used to coagulate rubber from the latex. Acetone is made from acetic acid. *Sugar of lead*, $(CH_3COO)_2Pb + 3H_2O$, is used in medicine and dyeing.

Propionic acid, CH_3CH_2COOH, occurs in traces in pyroligneous acid. It is made by oxidising normal propyl alcohol with $K_2Cr_2O_7$ and H_2SO_4.

$$\underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} + 2O = \underset{\text{Propionic acid}}{CH_3CH_2COOH} + H_2O.$$

It is a liquid (b.p. 141°) with a pungent smell, resembling acetic acid in its properties. It mixes with alcohol, water or ether in all proportions. From aqueous solution, it separates as an oil on adding solid $CaCl_2$, whence the name which means 'first fat'. Calcium propionate is added to bread dough to prevent moulding.

Butyric acid, C_3H_7COOH, exists in two isomeric forms, normal and iso-, both occur in nature. The normal acid, $CH_3.CH_2.CH_2.COOH$, is present in butter as a glyceride; rancid butter contains the free acid. By fermenting sugars such as glucose, or starch with *Bacillus butylicus*, present in sour milk or rancid cheese, butyric acid is obtained, lactic acid being formed first:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} = \underset{\text{Lactic acid}}{2C_3H_6O_3}.$$

$$\underset{\text{Lactic acid}}{2C_3H_6O_3} = \underset{n\text{-Butyric acid}}{CH_3—CH_2—CH_2—COOH} + 2CO_2 + 2H_2.$$

n-Butyric acid is a thick, colourless liquid (b.p. 162°) with a smell of rancid butter or stale perspiration. It is soluble in water and volatile in steam. Ethyl butyrate smells like pine-apple, it is an artificial essence. The acid is used to remove lime from leather.

Iso-butyric acid, $(CH_3)_2CH.COOH$, occurs in some plants and is made by oxidising isobutyl alcohol, $(CH_3)_2CHCH_2OH$. It is a liquid (b.p. 154°), very slightly soluble in water.

Higher fatty acids.—The most commonly occurring acids in natural fats and oils from animal and vegetable sources are oleic, palmitic and stearic acids. As already mentioned, they are present as glycerides *i.e.*, as glycerine esters. It is note-worthy that usually 'mixed' glycerides occur in nature, that is to say, of the three –OH groups in glycerol, one may be occupied by stearic acid, another by oleic acid and the third possibly by palmitic acid. These fatty acids are important as their sodium salts make soaps. Stearic acid, mixed with paraffin wax, is employed in making candles. Glyceride of oleic acid predominates in olive oil, that of palmitic acid in palm oil while the main constituent of lard and tallow is the glyceride of stearic acid. Zinc stearate is used in certain ointments. Copper salts of these acids are effective fungicides.

Palmitic acid, $C_{15}H_{31}COOH$, is a waxy solid (m.p 63°) as also *stearic acid*, $C_{17}H_{35}.COOH$, (m.p. 69°) while *oleic acid*, $C_{17}H_{33}COOH$, is an oily liquid. The first two of these are saturated while oleic acid contains a double bond. On hydrogenation, oleic acid passes on to stearic acid. These acids are highly soluble in alcohol but insoluble in water.

General methods of preparation of fatty acids.—(1) By the oxidation of primary alcohols, or of aldehydes and ketones, say with $K_2Cr_2O_7$ and H_2SO_4:

$$\underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{O} \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{O} \underset{\text{Formic acid}}{HCOOH}.$$

(*ii*) By the hydrolysis of alkyl cyanides:

$$\underset{\text{Methyl cyanide}}{CH_3CN} + 2H_2O = \underset{\text{Acetic acid}}{CH_3COOH} + NH_3.$$

(*iii*) By heating di-carboxylic acids containing two –COOH groups attached to the *same* carbon atom:

$$\underset{\text{Malonic acid}}{HOOC.CH_2.COOH} \longrightarrow \underset{\text{Acetic acid}}{CH_3.COOH} + CO_2.$$

$$\underset{\text{Oxalic acid}}{HOOC{-}COOH} \longrightarrow \underset{\text{Formic acid}}{HCOOH} + CO_2.$$

(*iv*) By hydrolysing esters with mineral acids or alkalis. Higher fatty acids are conveniently obtained by this method from natural fats and oils.

$$\underset{\text{Methyl ester of a fatty acid}}{RCOO.CH_3} + H_2O = \underset{\text{Fatty acid}}{RCOOH} + \underset{\text{Methyl alcohol}}{CH_3OH}.$$

General properties.—The lower members are corrosive liquids with a pungent smell and sour taste; they are soluble in water, turn litmus red and are also volatile in steam. They are colourless and highly soluble in alcohol and ether.

Fatty acids form salts with alkalis as usual:

$$CH_3COO\boxed{H + HO}Na = \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O.$$

Metals like zinc liberate hydrogen from the lower members:

$$2CH_3COOH + Zn = \underset{\text{Zinc acetate}}{(CH_3COO)_2Zn} + H_2.$$

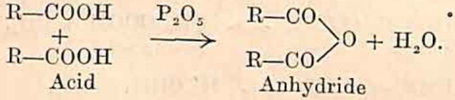
On heating with alcohols, fatty acids form *esters*; in presence of dehydrating agents, the reaction goes to completion.

$$\underset{\text{Acetic acid}}{CH_3COO}\overline{H + HO}\underset{\text{Alcohol}}{C_2H_5} \Longleftrightarrow \underset{\text{Ethyl acetate}}{CH_3COO.C_2H_5} + H_2O.$$

They react with PCl_5 and give *acid chlorides,* the $-OH$ group being thus replaced by a chlorine atom:

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 = \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl.$$

By the action of dehydrating agents such as phosphorus pentoxide, P_2O_5, higher fatty acids form *anhydrides,* one mol. of water being thus eliminated from two mols. of the acid:



$$\underset{\text{Acid}}{\begin{array}{c} R\text{—}COOH \\ + \\ R\text{—}COOH \end{array}} \xrightarrow{P_2O_5} \underset{\text{Anhydride}}{\left.\begin{array}{l} R\text{—}CO \\ R\text{—}CO \end{array}\right\rangle O} + H_2O.$$

The alkali salts of fatty acids, on dry distillation with soda-lime, yield paraffins (p. 27).

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH = \underset{\text{Methane}}{CH_4} + Na_2CO_3.$$

On *dry distillation,* their calcium salts form ketones (p. 71); formic acid is, however, an exception:

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} = \underset{\text{Acetone}}{CH_3.CO.CH_3} + CaCO_3.$$

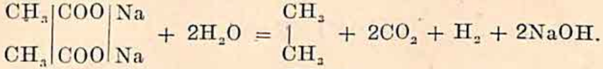
By heating calcium salt of a fatty acid with calcium formate, both dry, aldehydes result:

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium formate}}{(HCOO)_2Ca} = \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2CaCO_3.$$

Their ammonium salts, on heating in a sealed tube, form *amides:*

$$\underset{\text{Ammon. acetate}}{CH_3COONH_4} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O.$$

Alkali salts of fatty acids, on electrolysis, give paraffins (p. 30):



$$\begin{array}{l|l|l} CH_3 & COO & Na \\ CH_3 & COO & Na \end{array} + 2H_2O = \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + 2CO_2 + H_2 + 2NaOH.$$

Sodium acetate Ethane

Chlorine or bromine, in presence of sunlight and suitable catalysts, reacts with fatty acids liberating HCl or HBr. All the three H of the $-CH_3$ group can thus be replaced, trichloro-acetic acid, CCl_3COOH, being finally obtained from acetic acid.

$$CH_3COOH + Cl_2 = CH_2Cl.COOH + HCl.$$

Acetic acid Monochloro-acetic acid

Questions

1. How is acetic acid made on a large scale? Give its uses. Starting with acetic acid how would you prepare (a) acetic anhydride, (b) acetamide and (c) amino-acetic acid? I.Sc. 1953, Poona Uni.

2. Describe 'quick vinegar' process for making acetic acid. Starting from acetic acid, how will you obtain (a) formic acid, (b) acetone, (c) methyl alcohol? I.Sc. 1954, Nagpur Uni.

3. How would you distinguish, by physical and chemical tests, between ethyl alcohol, acetone and acetic acid?

4. How is formic acid manufactured? What are its uses?

5. By what tests formic acid can be distinguished from acetic acid?

CHAPTER XI

Derivatives of fatty acids.—Different types of derivatives may be obtained from fatty acids by replacing the hydrogen or hydroxyl group of the $-COOH$ group by an atom or radical, as well as by substituting the hydrogen of the alkyl group similarly. The following are examples:

$$\underset{\text{Acetic acid}}{CH_3COOH,}\quad \underset{\text{Sodium acetate}}{CH_3COONa,}\quad \underset{\text{Acetyl chloride}}{CH_3COCl,}\quad \underset{\text{Acetic anhydride}}{(CH_3CO)_2O,}$$

$$\underset{\text{Acetamide}}{CH_3CONH_2,}\quad \underset{\text{Chloro-acetic acid}}{CH_2Cl.COOH,}\quad \underset{\text{Cyanacetic acid}}{CH_2.CN.COOH.}$$

Acid chlorides, R.COCl, are formed when the $-OH$ of the $-COOH$ group is replaced by a chlorine atom. This is usually effected by phosphorus penta- or tri-chloride or thionyl chloride, $SOCl_2$. In all cases, HCl is evolved. Thionyl chloride is cheaper and also more convenient to use. Salts of acids, which are less costly, are usually employed, they react similarly. *Formyl chloride, HCOCl, is unknown.*

Acetyl chloride, CH_3COCl, is made in the laboratory by heating, on a water-bath, *glacial* acetic acid and phosphorus trichloride, PCl_3, which is slowly added from the tap-funnel to the acid in the flask. A soda-lime tower absorbs the HCl formed, and also prevents the entry of moisture into the receiver from the air. Acetyl chloride distils into the receiver.

$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 = \underset{\text{Acetyl chloride}}{3CH_3COCl} + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

Commercially, sodium acetate and a mixture of SO_2 and Cl_2 are employed.

$$\underset{\text{Sodium acetate}}{CH_3COONa} + SO_2Cl_2 = \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_3 + NaCl.$$

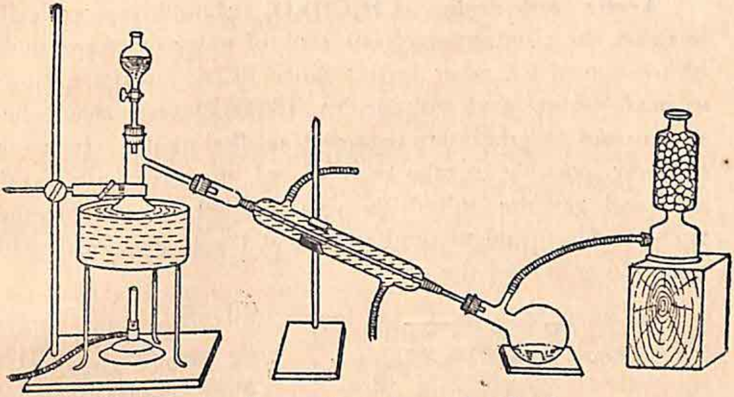


Fig. 31.—Preparation of acetyl chloride.

Properties.—Acetyl chloride is a colourless, fuming liquid (b.p. 55°). It is *rapidly* decomposed by water into acetic acid.

$$\mathrm{CH_3CO}\underline{|\overline{\mathrm{Cl + H}}|}\mathrm{OH = CH_3COOH + HCl.}$$

Acetyl chloride Acetic acid

With alcohols, it forms esters:

$$\mathrm{CH_3CO}\underline{|\overline{\mathrm{Cl + H}}|}\mathrm{O.C_2H_5 = CH_3COO.C_2H_5 + HCl.}$$

Acetyl chloride Alcohol Ethyl acetate

Acetyl chloride reacts with ammonia to form acetamide:

$$\mathrm{CH_3CO}\underline{|\overline{\mathrm{Cl + H}}|}\mathrm{NH_2 = CH_3CO.NH_2 + HCl.}$$

Acetyl chloride Acetamide

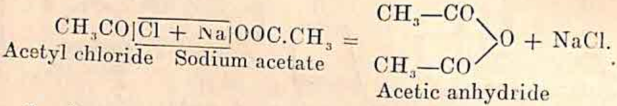
On heating with fused sodium acetate, acetyl chloride gives acetic anhydride:

$$\mathrm{CH_3.CO}\underline{|\overline{\mathrm{Cl + Na}}|}\mathrm{OOC.CH_3 = CH_3.CO.O.OC.CH_3 + NaCl.}$$

Acetyl chloride Sodium acetate Acetic anhydride

Acetyl chloride reacts with compounds having a hydroxyl group to form acetyl derivatives which are useful for their detection. Acetyl chloride is thus a valuable laboratory reagent. HCl is invariably evolved in such cases. The process is commonly called *acetylation*.

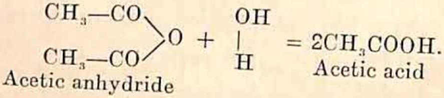
Acetic anhydride, $(CH_3CO)_2O$, should theoretically form by the elimination of one mol. of water from two mols. of acetic acid (*cf.* ether p. 61). Since RCO – group is known as *acyl* group, acid anhydrides, $(RCO)_2O$, are also called *acyl oxides* as ethers are regarded as alkyl oxides. It is not, however, possible to take away a mol. of water from acetic acid and get the anhydride with the help of dehydrating agents. The usual method is to heat the acid chloride with the sodium salt of the acid:



$$\underset{\text{Acetyl chloride}}{CH_3CO}\boxed{Cl + Na}\underset{\text{Sodium acetate}}{OOC.CH_3} = \underset{\text{Acetic anhydride}}{\left.\begin{matrix}CH_3-CO \\ CH_3-CO\end{matrix}\right\rangle O} + NaCl.$$

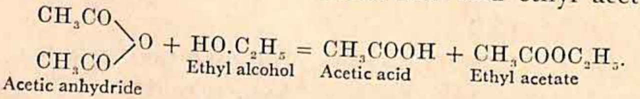
Powdered, fused sodium acetate with almost an equal weight of acetyl chloride (added gradually) is shaken at ordinary temperature and distilled. Acetic anhydride goes over at about 140°.

Properties.—Acetic anhydride is a colourless, neutral liquid with a pungent odour; it boils at 137° and is slightly heavier than water. It *slowly* reacts with water giving two mols. of acetic acid:



$$\underset{\text{Acetic anhydride}}{\left.\begin{matrix}CH_3-CO \\ CH_3-CO\end{matrix}\right\rangle O} + \begin{matrix}OH \\ | \\ H\end{matrix} = \underset{\text{Acetic acid}}{2CH_3COOH.}$$

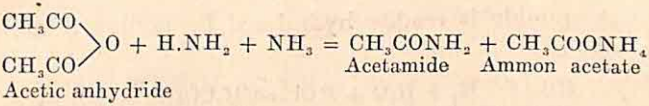
With ethyl alcohol, it forms acetic acid and ethyl acetate:



$$\underset{\text{Acetic anhydride}}{\left.\begin{matrix}CH_3CO \\ CH_3CO\end{matrix}\right\rangle O} + \underset{\text{Ethyl alcohol}}{HO.C_2H_5} = \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}.$$

Like acetyl chloride, acetic anhydride is widely used for the detection and estimation of hydroxyl groups in organic compounds.

Ammonia and acetic anhydride react readily forming acetamide and ammonium acetate:



$$\underset{\text{Acetic anhydride}}{\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>\!O} + H.NH_2 + NH_3 = \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Ammon acetate}}{CH_3COONH_4}$$

Formic anhydride, like formyl chloride, is unknown.

Acid amides are derivatives of acids obtained by replacing the -OH group by an $-NH_2$ group; they may, therefore, be written as $RCO.NH_2$. But direct replacement is not possible; the usual procedure is to distil ammonium salts of fatty acids. The basic character of the $-NH_2$ group has largely disappeared due to the influence of the $>CO$ group; amides are almost neutral. They form unstable salts with strong acids and also yield metallic salts *e.g.*, mercury acetamide, $(CH_3CONH)_2Hg$ with HgO.

Formamide, $HCONH_2$, is made by heating ammonium formate with ammonia gas:

$$\underset{\text{Ammonium formate}}{HCOONH_4} \rightleftharpoons \underset{\text{Formamide}}{HCONH_2} + H_2O$$

It is a colourless liquid (b.p. 200°), readily soluble in water and alcohol.

Acetamide, CH_3CONH_2, is prepared by distilling ammonium acetate with glacial acetic acid which improves the yield. The distillate above 213° is collected.

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \rightleftharpoons \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

It may also be obtained by reacting ethyl acetate or acetyl chloride with concentrated ammonia:

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NH_3 = C_2H_5OH + CH_3CONH_2.$$

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + 2NH_3 = NH_4Cl + \underset{\text{Acetamide}}{CH_3CONH_2}.$$

It is a colourless, crystalline solid (m.p. 82°, b.p. 222°), highly soluble in water, alcohol, and ether. The impure product smells of mice but the pure stuff is odourless.

Acetamide is readily hydrolysed by boiling dilute acids or alkalis.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + H_2O + HCl = \underset{\text{Acetic acid}}{CH_3COOH} + NH_4Cl.$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} + NaOH = \underset{\text{Sodium acetate}}{CH_3COONa} + NH_3.$$

With nitrous acid, it gives acetic acid, nitrogen and water:

$$\underset{\text{Acetamide Nitrous acid}}{CH_3CON\boxed{H_2 + O}NOH} = \underset{\text{Acetic acid}}{CH_3COOH} + H_2O + N_2.$$

Distilled with strong dehydrating agents such as phosphorus pentoxide, acetamide yields methyl cyanide.

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Methyl cyanide}}{CH_3CN} + H_2O.$$

Sodium and alcohol reduce it to ethylamine:

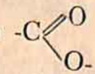
$$\underset{\text{Acetamide}}{CH_3CONH_2} + 4H = \underset{\text{Ethylamine}}{CH_3.CH_2.NH_2} + H_2O.$$

These reactions enable us to obtain new compounds from fatty acids. They are, therefore, important.

Esters.—When an alcohol reacts with an acid, organic or inorganic, we get an *ester* and water much in the same way as a caustic alkali produces a salt and water with an acid:

$$\underset{\text{Acetic acid Ethyl alcohol}}{CH_3CO\boxed{OH + H}O.C_2H_5} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COO.C_2H_5} + H_2O$$

$$\underset{\text{Nitric acid Ethyl alcohol}}{O_2N\boxed{OH + H}O.H_5C_2} \rightleftharpoons \underset{\text{Ethyl nitrate}}{O_2N.O.C_2H_5} + H_2O$$

Organic *esters e.g.,* those obtained from alcohols and fatty acids, have the group  linked to two alkyl radicals. They are thus represented by the general formula R.CO.O.R′. Esters are named from the acid and alkyl radical, the alcoholic radical comes first, *e.g.,* ethyl acetate, $CH_3COO.C_2H_5$, ethyl hydrogen sulphate, $C_2H_5.HSO_4$, and so on. One interesting fact in connection with the *esterification process i.e.,* the formation of esters from alcohols and acids directly, is that the reaction is balanced or reversible and comes to a stop usually when about $^2/_3$ of each have taken part in the reaction. For better yield, therefore, some dehydrating agent has to be used in order to take away the water formed. Conc. H_2SO_4, HCl gas, $ZnCl_2$, etc., are generally employed for this purpose.

Ethyl acetate, $CH_3COO.C_2H_5$, which occurs in various fruits, may be prepared by heating together ethyl alcohol, glacial acetic acid and conc. H_2SO_4 in a distilling flask. H_2SO_4 takes away the water formed. It is a colourless, pleasant smelling liquid (b.p. 77°), lighter than water and slightly soluble in it. It is used as a solvent, in organic synthesis and in making antipyrin, a drug.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Acetic acid}}{CH_3COOH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Organic esters are obtained in good yield by reacting acid chlorides with alcohols (p. 85).

$$\underset{\text{Acetyl chloride}}{CH_3CO}\boxed{Cl + H}\underset{\text{Alcohol}}{O.C_2H_5} = \underset{\text{Ethyl acetate}}{CH_3CO.O.C_2H_5} + HCl.$$

Some esters are artificial flavouring agents *e.g.,* ethyl butyrate has the odour of pineapple. Ethyl acetate is a stimulant in medicine under the name 'acetic ether'.

Esters are *slowly* decomposed by water (hydrolysis) into the original alcohol and acid. The process is accelerated by dilute mineral acids or alkalis. Ethyl acetate breaks up into alcohol and acetic acid. This is also called *saponification* as soap is made by alkaline hydrolysis of an ester (oil).

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O = \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}.$$

With concentrated ammonia, it forms acetamide (difference from inorganic esters):

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NH_3 = \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Alcohol}}{C_2H_5OH}.$$

By the action of PCl_5, ethyl acetate gives acetyl chloride and ethyl chloride:

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + PCl_5 = \underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3.$$

Esters of inorganic acids are obtained in the same way as organic esters. Thus, **ethyl hydrogen sulphate, $C_2H_5.HSO_4$**, is prepared by heating on water-bath equal volumes of alcohol and conc. H_2SO_4 for about an hour.

$$\underset{\text{Alcohol}}{C_2H_5OH} + H_2SO_4 \rightleftharpoons \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5.HSO_4} + H_2O$$

Ethyl hydrogen sulphate is a thick liquid, sour to the taste and like inorganic bisulphates, gives an acid reaction and decomposes carbonates. It readily reacts with boiling water, alcohol and H_2SO_4 as follows:

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5.HSO_4} + H_2O \Longleftrightarrow \underset{\text{Alcohol}}{C_2H_5OH} + H_2SO_4$$

$$C_2H_5.HSO_4 + \underset{\text{Alcohol}}{C_2H_5OH} = \underset{\text{Ether}}{C_2H_5.O.C_2H_5} + H_2SO_4.$$

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5.HSO_4} + H_2SO_4 = \underset{\text{Ethylene}}{C_2H_4} + 2H_2SO_4.$$

Nitro-paraffins, R.NO$_2$, are obtained by the substitution of a hydrogen atom in the paraffin molecule by the nitro group, $-NO_2$. Nitromethane is $CH_3.NO_2$. It is isomeric with methyl nitrite, CH_3-O-NO, an ester, derived from methyl alcohol and nitrous acid. In nitro-paraffins, the nitrogen atom is *directly* linked to carbon while in alkyl nitrites, oxygen forms a bridge between them.

Nitro-methane (or nitro-ethane) may be prepared by distilling methyl (or ethyl) iodide with silver nitrite.

$$\underset{\text{Methyl iodide}}{CH_3\overline{|I} + \underset{\text{Silver nitrite}}{\overline{Ag|}NO_2}} = \underset{\text{Nitromethane}}{CH_3.NO_2} + AgI.$$

Both nitro-methane (b.p. 101°) and nitro-ethane (b.p. 114°) are colourless, pleasant-smelling, inflammable liquids, insoluble in water.

In is rather peculiar that we obtain methyl (or ethyl) nitrite instead of nitro-methane (or nitro-ethane) if we employ any other metallic nitrite in place of silver nitrite.

With caustic alkali, nitro-methane forms salt and water (methyl nitrite is thus hydrolysed to alcohol and acid as is usual with esters):

$$\underset{\text{Nitro-methane}}{CH_3NO_2} + KOH = \underset{\text{Pot. nitromethane}}{CH_2KNO_2} + H_2O.$$

On reduction, nitromethane gives methylamine:

$$\underset{\text{Nitromethane}}{CH_3NO_2} + 6H = \underset{\text{Methylamine}}{CH_3NH_2} + 2H_2O.$$

Methyl or *ethyl nitrite* is prepared by the action of KNO_2 and dilute HCl on the alcohol *in the cold.* Ethyl nitrite, $C_2H_5NO_2$, boils at 16° and smells like apples.

Oils and fats.—Oils and fats are glycerine esters of higher fatty acids (p. 80) as ethyl acetate is an ethyl alcohol ester of acetic acid. They are consequently called 'glycerides' in order to distinguish them from mineral oils which are hydrocarbons (*e.g.*, kerosene, petrol) as well as essential oils such as turpentine or clove oil, which are aromatic *i.e.*, closed-chain compounds. They are also called 'fixed oils' as they cannot ordinarily be distilled off. Like other esters, glycerides are readily hydrolysed by alkalis to glycerol and fatty acids; sodium salts of these acids are *soaps.*

Chemically speaking, there is *no difference* between fats and oils; fats are harder in consistency than oils. Glycerides melting above 20° are usually termed fats while those melting below this temperature are commonly known as oils. In our country, cocoanut oil is an oil in summer but may become a 'fat' in winter. Oils and fats are derived from vegetables as well as animals. By mechanically crushing the seeds, oil may be extracted; this can more effectively be done by means of fat solvents such as benzene, carbon tetrachloride, etc. By boiling the chopped animal tissues with water, fats may be separated.

Natural fats and oils are neutral and lighter than water in which they are insoluble. A popular saying 'Oil will not mix with water' roughly defines an oil. They are, however, readily soluble in benzene, acetone, ether, carbon tetrachloride, etc. The glycerides of saturated higher fatty acids are generally solids whilst those of unsaturated acids are liquids. Some oils, *e.g.*, linseed oil, slowly absorb oxygen from the air when exposed in thin layers and form a dry resinous film. This is utilised in the paint industry and also in making oilcloth. These are called *drying oils.*

One common method of converting liquid oils into solid fats is to add hydrogen to the double bond of unsaturated fatty acids in presence of a catalyst. This is called hydrogenation or hardening of oils. Vegetable ghee or *Vanaspati* is thus made in our country in fairly large quantities now. In 1950, India produced 171,600 tons of Vanaspati, mostly from groundnut oil.

Soaps.—Alkali salts of higher fatty acids are known as soaps. Sodium salts give hard soaps, while potassium salts make soft soaps. Toilet and ordinary washing soaps are all hard soaps. A suitable mixture of oils and fats is treated with caustic soda solution in a steam-heated kettle whereby sodium salts and water are formed. By adding common salt to this mixture, soap is precipitated or 'salted' out, glycerine remains in the mother-liquor ('sweet water').

$$\underset{\text{Tristearin (glyceride)}}{C_3H_5(C_{17}H_{35}COO)_3} + 3NaOH = \underset{\text{Glycerol}}{C_3H_5(OH)_3} + \underset{\text{Sodium stearate (soap)}}{3C_{17}H_{35}COONa}.$$

It is dried, dyed, perfumed and made into cakes. Floating soaps are made by blowing air through molten soap whereby it becomes lighter than water. Transparent soaps are made by dissolving soap in methylated spirit and driving off the alcohol. Cold process soaps are made from tallow and cocoanut oil and warm NaOH without heating the mixture ; the glycerine remains with the soap. In 1951 India produced 79300 tons of soap, in 1952-53 she exported 26,001 cwt. of it.

Monocholoro-acetic acid, $CH_2Cl.COOH$, is a derivative of acetic acid in which the -COOH group remains intact but a hydrogen of the alkyl group is replaced by a Cl atom. It is made by passing chlorine gas into boiling acetic acid in presence of a little iodine or sulphur until the requisite increase in weight is attained:

$$\underset{\text{Acetic acid}}{CH_3COOH} + Cl_2 = \underset{\text{Mono-chloroacetic acid}}{CH_2ClCOOH} + HCl.$$

It is a colourless, crystalline solid (m.p. 62°), soluble in water. The acid is corrosive and is much stronger than acetic acid. It is used in making glycine and synthetic indigo. With alcoholic ammonia, amino-acetic acid or glycine is obtained from monochloro-acetic acid:

$$\underset{\text{Chloro-acetic acid}}{CH_2ClCOOH} + 2NH_3 = \underset{\text{Amino-acetic acid}}{CH_2(NH_2)COOH} + NH_4Cl.$$

By heating with *moist* silver oxide, glycollic acid results:

$$CH_2Cl.COOH + AgOH = \underset{\text{Glycollic acid}}{CH_2(OH)COOH} + AgCl.$$

Amino-acetic acid, $CH_2(NH_2)COOH$, as mentioned above, is obtained from chloro-acetic acid and ammonia ; it is acetic acid with one hydrogen atom of the methyl group replaced by an amino-group, $-NH_2$. Amino-acids are very important as they are the building stones of animal and vegetable proteins, so essential for our existence. Some 25 amino-acids have so far been obtained by the hydrolysis of proteins. Amino-acetic acid (or glycine) may be prepared by boiling glue or gelatine with dilute H_2SO_4 or NaOH. It is a colourless, crystalline solid (m.p. 236° with decomposition), readily soluble in water. It gives a deep red coloration with ferric chloride solution. It has a sweet taste whence the name glycocoll (*glykus*, sweet ; *kolla*, glue).

It is amphoteric *i.e.*, behaves both like an acid, forming salt with alkali (the -COOH group takes part) and also as a base, giving a salt with acids (the amino-group, $-NH_2$, participates).

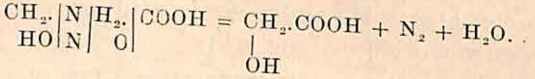
$$\underset{\text{Amino-acetic acid}}{CH_2(NH_2)COOH} + NaOH = \underset{\text{Sodium amino-acetate}}{CH_2(NH_2)COONa} + H_2O.$$

$$\underset{\text{Glycine}}{CH_2(NH_2)COOH} + HCl = \underset{\text{Glycine hydrochloride}}{Cl.H_3.N.CH_2COOH.}$$

The copper salt of glycine is deep blue and sparingly solube in water. Heated with soda-lime, glycine splits up into methylamine and CO_2:

$$\underset{\text{Glycine}}{CH_2(NH_2)COOH} = \underset{\text{Methylamine}}{CH_3NH_2} + CO_2.$$

Nitrous acid decomposes it into glycollic acid, nitrogen and water:



$$\begin{array}{l|l|l|l} CH_2. & N & H_2. & COOH \\ HO & N & O & \end{array} = \underset{\displaystyle OH}{\underset{|}{CH_2}}.COOH + N_2 + H_2O.$$

Glycollic acid

This reaction is quantitative and by measuring the volume of N_2 evolved, an amino-acid may be estimated.

Questions

1. Write short notes on : polymerisation, isomerism, substitution and additive products, and saponification. I.Sc. 1952, Nagpur Uni.

2. 0·180 g. of an organic compound gave 0·264 g. CO_2 and 0·108 g. H_2O. Its vapour density is 30. On boiling with NaOH solution, it gave methyl alcohol and sodium salt of the acid. What is its molecular formula? Give its structural formula and name it.
I.Sc. 1953, Bombay Uni.

3. How is acetamide made? How can you obtain acetic acid, ethylamine and methyl cyanide from it?

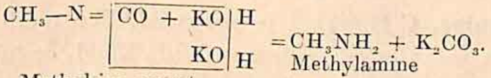
4. Write down, with equations, the action of ammonia on acetic acid, acetic anhydride, acetyl chloride, ethyl iodide and ethyl acetate.

5. How do you distinguish between methyl nitrite and nitromethane?

CHAPTER XII

Aliphatic amines, R.NH$_2$.— If one, two or all the hydrogen atoms of ammonia be replaced by alkyl groups such as methyl, -CH_3, ethyl, -C_2H_5, etc., we get aliphatic amines. Methylamine is CH_3NH_2, ethylamine has the formula, $C_2H_5NH_2$; these are primary amines. Dimethylamine, $(CH_3)_2NH$, and trimethylamine, $(CH_3)_3N$, are secondary and tertiary amines respectively. These are important as organic bases which are almost invariably derivatives of ammonia. Alkyl amines are stronger bases than ammonia, the strength increasing with the number of alkyl groups. We shall study the first two members, *viz.*, methylamine and ethylamine. They are typical of the family of amines.

Methylamine, CH_3NH_2, is a decomposition product of proteins and some alkaloids ; it occurs in the brine (common salt solution) in which herring fish has been salted. It may be prepared by boiling methyl iso-cyanate with caustic potash, the amine escapes as a gas.



$$CH_3{-}N{=}\boxed{\begin{array}{r}CO + KO \\ KO\end{array}}\begin{array}{l}H\\H\end{array} = \underset{\text{Methylamine}}{CH_3NH_2} + K_2CO_3.$$

Methyl iso-cyanate

It may as well be obtained from acetamide, bromine and KOH (*Hofmann's reaction*):

(*i*) $\underset{\text{Acetamide}}{CH_3.CO.NH_2} + Br + KOH = \underset{\text{Aceto-bromamide}}{CH_3CONHBr} + KBr + H_2O.$

(*ii*) $\underset{\text{Aceto-bromamide}}{CH_3CON\boxed{HBr + KOH}} = \underset{\text{Methyl iso-cyanate}}{CH_3NCO} + KBr + H_2O.$

(*iii*) $\underset{\text{Methyl isocyanate}}{CH_3NCO} + 2KOH = \underset{\text{Methylamine}}{CH_3NH_2} + K_2CO_3.$

Methylamine is also obtained by heating a mixture of formalin and ammonium chloride:

$$2HCHO + NH_4Cl = CH_3NH_2HCl + HCOOH$$

Methylamine is a colourless gas with an ammoniacal but fishy odour. Unlike ammonia, it burns in air with a yellow flame. Methylamine is highly soluble in water; the aqueous solution is alkaline to litmus.

Reactions.—(1) Methylamine fumes with HCl gas, like ammonia, to form the hydrochloride:

$$\underset{\text{Methylamine}}{CH_3NH_2} + HCl = \underset{\text{Methylamine hydrochloride}}{CH_3NH_3Cl.}$$

(2) Nitrous acid splits it up into methyl alochol, N_2 and water (*cf.* action of HNO_2 on NH_3).

$$\begin{array}{c|c|c} CH_3 & N & H_2 \\ OH & N & O \end{array} = \underset{\text{Methyl alcohol}}{CH_3OH} + N_2 + H_2O$$

$$\underset{\text{Ammonium nitrite}}{\begin{array}{c|c|c} H & N & H_2 \\ HO & N & O \end{array}} = H_2O + N_2 + H_2O.$$

(3) On heating with chloroform and alcoholic potash, methyalmine (or any primary amine) forms an isocyanide or carbylamine with intolerable smell (p. 47).

$$\underset{\text{Methylamine}}{CH_3NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH = \underset{\text{Methyl isocyanide}}{CH_3NC} + 3KCl + 3H_2O.$$

Ethylamine, $C_2H_5NH_2$, is prepared, like methylamine, (*i*) by hydrolysing ethyl isocyanate with KOH, or (*ii*) by the action of bromine and potash on propionamide.

$$\text{(i)}\quad \underset{\text{Ethyl isocyanate}}{C_2H_5NCO} + 2KOH = \underset{\text{Ethylamine}}{C_2H_5NH_2} + K_2CO_3.$$

$$(ii)\quad \underset{\text{Propionamide}}{C_2H_5CONH_2} \xrightarrow{Br + KOH} \underset{\text{Propion-bromamide}}{C_2H_5CONHBr} \xrightarrow{KOH}$$

$$\underset{\text{Ethyl isocyanate}}{C_2H_5NCO} \xrightarrow{KOH} \underset{\text{Ethylamine}}{C_2H_5NH_2.}$$

Ethylamine is a colourless, volatile and inflammable liquid (b.p. 19°) with a fishy but ammoniacal smell. It is highly soluble in water and has a biting taste. In its chemical behaviour, it strinkingly resembles methylamine.

The hydrochloride and the sulphate are $C_2H_5NH_3Cl$ and $(C_2H_5NH_3)_2SO_4$ respectively, made by direct union with the acids. Like methylamine, ethylamine gives ethyl alcohol, N_2 and water with nitrous acid. Both methyl- and ethylamine react with acetyl chloride or acetic anhydride to give crystalline derivatives by which the amines are detected.

$$\underset{\text{Methylamine}}{CH_3NH_2} + \underset{\text{Acetyl chloride}}{CH_3COCl} = \underset{\text{Methyl acetamide}}{CH_3NH.CO.CH_3} + HCl.$$

$$\underset{\text{Ethylamine}}{2C_2H_5NH_2} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} = \underset{\text{Ethyl acetamide}}{2C_2H_5NH.CO.CH_3} + H_2O.$$

With alkyl iodides, both methyl- and ethylamine produce secondary and tertiary amines on heating:

$$\underset{\text{Methylamine}}{CH_3NH_2} + \underset{\text{Methyl iodide}}{CH_3I} = \underset{\text{Dimethylamine hydriodide}}{(CH_3)_2.NH_2I.}$$

General methods of preparation.—(*i*) By the reduction of nitro-paraffins with tin and HCl (p. 91).

$$\underset{\text{Nitro-ethane}}{C_2H_5NO_2} + 6H = \underset{\text{Ethylamine}}{C_2H_5NH_2} + 2H_2O.$$

(*ii*) From alkyl cyanides by reduction with sodium and alcohol.

$$\underset{\text{Methyl cyanide}}{CH_3CN} + 4H = \underset{\text{Ethylamine}}{CH_3CH_2NH_2.}$$

(*iii*) By passing alcohol vapour with ammonia over gently heated thoria:

$$\underset{\text{Methyl alcohol}}{CH_3OH} + NH_3 = \underset{\text{Methylamine}}{CH_3NH_2} + H_2O.$$

(*iv*) Heated under pressure in a sealed tube, alkyl halides and alcoholic ammonia form alkylamines. But primary, secondary, tertiary amines together with other more complex bodies are simultaneously formed; these are not easy to separate.

Amines like ammonia are basic anhydrides which give the true base with water:

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4{}^+ + OH^-$$

$$CH_3NH_2 + H_2O \rightleftarrows CH_3NH_3OH \rightleftarrows CH_3NH_3{}^+ + OH^-$$

Unlike ammonia, amines burn in air with a yellow flame. They form crystalline salts with acids.

Questions

1. Give as many methods as you can for preparing a primary amine. How is a primary amine distinguished from a secondary and a tertiary amine? Give equations. I.Sc. 1950, Nagpur Uni.

2. How do amides differ from amines? Describe the methods for the preparation of acetamide and methylamine. Give important chemical reactions of these two compounds. I.Sc. 1954, Nagpur Uni.

3. What are the general methods of preparing primary amines? Give an equation in each case.

4. What is carbylamine reaction? Can this be done with iodoform? What is the action of HNO_2 on ethylamine and acetamide?

CHAPTER XIII

Cyanogen compounds.—Organic compounds containing the univalent cyanogen group, $-CN$, are important in the synthesis of new derivatives. We have already come across methyl and ethyl cyanide (pp. 97, 46) and seen how they can be converted into corresponding amines by reduction. The mother substance in organic cyanides is cyanogen, $(CN)_2$, which occurs in coal gas and blast furnace gases in traces.

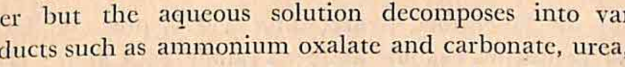
Cyanogen, $(CN)_2$, was first prepared by Gay-Lussac by heating silver cyanide:

$$\underset{\text{Silver cyanide}}{2AgCN} = 2Ag + \underset{\text{Cyanogen}}{(CN)_2}.$$

It is, however, more conveniently made by warming concentrated solutions of copper sulphate and potassium cyanide:

$$\underset{\text{Pot. cyanide}}{4KCN} + \underset{\text{Copper sulphate}}{2CuSO_4} = 2K_2SO_4 + \underset{\text{Cuprous cyanide}}{Cu_2(CN)_2} + \underset{\text{Cyanogen}}{(CN)_2}.$$

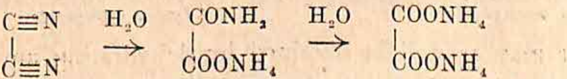
Cyanogen may as well be prepared by distilling anhydrous ammonium oxalate with phosphorus pentoxide; it is a case of dehydration:



$$\begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix} \xrightarrow{-2H_2O} \begin{matrix} CONH_2 \\ | \\ CONH_2 \end{matrix} \xrightarrow{-2H_2O} \begin{matrix} C{\equiv}N \\ | \\ C{\equiv}N. \end{matrix}$$

Ammon. oxalate Oxamide Cyanogen

Cyanogen is a colourless, *extremely poisonous* gas smelling like crushed bitter-almonds. It is fairly soluble in water but the aqueous solution decomposes into various products such as ammonium oxalate and carbonate, urea, etc. The gas burns in air with a violet flame, forming CO_2 and N_2. On heating, it polymerises into a brown powder, paracyanogen, $(CN)_n$. Mineral acids such as HCl hydrolyse it to oxamide and then into ammonium oxalate:



$$\begin{matrix} C{\equiv}N \\ | \\ C{\equiv}N \end{matrix} \xrightarrow{H_2O} \begin{matrix} CONH_2 \\ | \\ COONH_4 \end{matrix} \xrightarrow{H_2O} \begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix}$$

Cyanogen Oxamide Ammon. oxalate

Likewise cyanides—aliphatic or aromatic—are hydrolysed to carboxylic acids:

$$\underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{H_2O} \underset{\text{Acetic acid}}{CH_3COOH}.$$

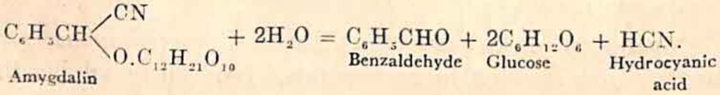
It is useful in introducing a new carbon atom or a carboxyl group into an organic compound—a job which may be otherwise difficult. Alkyl cyanides are sometimes called *nitriles* of acids they give on hydrolysis. *Acetonitrile* is another name for methyl cyanide. Passed into KOH solution, cyanogen forms pot. cyanide and cyanate, like chlorine:

$$2KOH + (CN)_2 = KCN + KCNO + H_2O.$$

$$2KOH + Cl_2 = KCl + KClO + H_2O.$$

A strong solution of KOH is thus a good absorbent for cyanogen gas.

Hydrocyanic acid, HC≡N, is the simplest of cyanogen compounds and also the simplest organic acid. Scheele first obtained it by heating Prussian blue with H_2SO_4, hence the alternate name *prussic acid*. In combined state, it occurs in bitter almonds as *amygdalin*, a glucoside, from which it can be obtained by hydrolysis. Compounds of glucose are called *glucosides*.



$$\underset{\text{Amygdalin}}{C_6H_5CH\left\langle\begin{matrix}CN\\ O.C_{12}H_{21}O_{10}\end{matrix}\right.} + 2H_2O = \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Glucose}}{2C_6H_{12}O_6} + \underset{\text{Hydrocyanic acid}}{HCN}.$$

In the laboratory, hydrocyanic acid is prepared by distilling potassium cyanide or ferrocyanide with *dilute* H_2SO_4 in a fume chamber.

$$\underset{\text{Pot. cyanide}}{2KCN} + H_2SO_4 = K_2SO_4 + \underset{\text{Hydrocyanic acid}}{2HCN}.$$

$$\underset{\text{Pot. ferrocyanide}}{2K_4Fe(CN)_6} + 3H_2SO_4 = 3K_2SO_4 + \underset{\text{Pot. ferrous errocyanide}}{K_2Fe.Fe(CN)_6} + 6HCN.$$

It may as well be obtained by dehydrating ammonium formate with phosphorus pentoxide:

$$\underset{\text{Ammon. formate}}{HCOONH_4} \xrightarrow{-H_2O} \underset{\text{Formamide}}{HCONH_2} \xrightarrow{-H_2O} \underset{\text{Hydrocyanic acid}}{HCN.}$$

Anhydrous HCN may be obtained by heating powdered KCN and pot. hydrogen sulphide, KSH:

$$KCN + KSH = K_2S + HCN$$

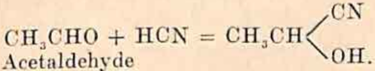
Properties.—Pure hydrocyanic acid is a colourless, highly volatile liquid (b.p. 26°) with the odour of crushed bitter almonds. It burns with a violet flame and is freely soluble in water and alcohol in any proportion. *The acid is a deadly poison.* It is a very weak acid indeed, even carbonic acid is about 500 times stronger than this. It is, therefore, slowly decomposed by water into formic acid:

$$\underset{\text{Hydrocyanic acid}}{HCN + 2H_2O} \Longleftrightarrow \underset{\text{Formic acid}}{HOOCH} + NH_3 \Longleftrightarrow \underset{\text{Ammon. formate}}{HCOONH_4}$$

On reduction with sodium amalgam and acetic acid, methylamine results from hydrocyanic acid:

$$HCN + 4H = \underset{\text{Methylamine}}{CH_3NH_2.}$$

It combines directly with aldehydes and ketones forming cyanhydrins (pp. 68, 72).



$$\underset{\text{Acetaldehyde}}{CH_3CHO} + HCN = \underset{\text{Acetaldehyde cyanhydrin}}{CH_3CH\begin{cases} CN \\ OH. \end{cases}}$$

The acid gives salts with caustic alkalis, whilst indirectly, an alkyl group may replace its hydrogen, forming alkyl cyanide:

$$H\overline{|CN + K|}OH = \underset{\text{Pot. cyanide}}{KCN} + H_2O. \quad K\overline{|CN + CH_3|}I = \underset{\text{Methyl cyanide}}{CH_3CN} + KI.$$

Hydrocyanic acid is used for killing insect pests in fruit-trees which are first covered with a cloth tent and then the gas is introduced. In Bombay, imported cotton is fumigated on the sea with HCN gas for killing boll-weevil. It is also used in medicine *in very minute doses.*

Alkyl cyanides, RCN, may be prepared by heating potassium cyanide with an alkyl halide in alcoholic solution.

$$\underset{\text{Methyl iodide}}{CH_3\boxed{I + K}CN} = \underset{\text{Methyl cyanide}}{CH_3.CN} + KI.$$

They may also be obtained by distilling ammonium salts of fatty acids with P_2O_5. It is a case of dehydration.

$$\underset{\text{Ammon. acetate}}{CH_3COONH_4} \xrightarrow{-H_2O} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{-H_2O} \underset{\text{Methyl cyanide}}{CH_3CN}.$$

Alkyl cyanides are colourless liquids with a sweet smell but are extremely poisonous. They are fairly soluble in water. On reduction, they yield primary amines:

$$\underset{\text{Ethyl cyanide}}{C_2H_5CN} + 4H = \underset{\text{Propylamine}}{C_2H_5.CH_2NH_2}.$$

On hydrolysis, they are first converted into amides and finally into acids:

$$\underset{\text{Methyl cyanide}}{CH_3CN} + H_2O = \underset{\text{Acetamide}}{CH_3CONH_2}$$

$$CH_3CONH_2 + H_2O = \underset{\text{Acetic acid}}{CH_3COOH} + NH_3 = \underset{\text{Ammon. acetate}}{CH_3COONH_4}$$

Ascent & descent in a homologous series.

(a) Methyl alcohol ⟶ Ethyl alcohol:

$$\underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{PI_3} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{H} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(b) Ethyl alcohol ⟶ Methyl alcohol:

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Ammon. acetate}}{CH_3COONH_4} \xrightarrow{-H_2O} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{KBrO}$$

$$\underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{HNO_2} \underset{\text{Methyl alcohol}}{CH_3OH}.$$

Questions

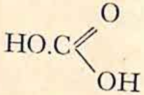
1. What group characterises an acid chloride, a nitrite, an amide and an anhydride? Give an example of each.

2. How can you convert acetic acid into methylamine and methyl cyanide into acetic acid?

3. What is the structural difference between a cyanide and an isocyamide? How do you distinguish between the two?

4. How is hydrocyanic acid prepared? What are its chief properties and uses?

CHAPTER XIV

Dibasic acids are compounds with *two* carboxyl groups, –COOH, per molecule. The simplest dibasic acid. *viz.*, carbonic acid, H_2CO_3, or  $HO.C\begin{smallmatrix}\nearrow O \\ \searrow OH\end{smallmatrix}$, does not, however, contain two independent carboxyl groups. The simplest dicarboxylic acid is oxalic acid, HOOC.COOH.

Oxalic acid, HOOC.COOH, occurs in plants of the *Oxalis* group as acid potassium salt, in sorrel, beet leaves and myrobalans ; calcium oxalate is present in some cell walls.

Preparation.—The laboratory method is to warm powdered cane-sugar with ten times its weight of conc. HNO_3 in a fume chamber. On concentrating and cooling the liquid, crystals of oxalic acid, $HOOC.COOH,2H_2O$, separate.

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + 9O_2 = \underset{\text{Oxalic acid}}{6(COOH)_2} + 5H_2O.$$

The commercial method naturally starts with a much cheaper material. Sawdust and conc. caustic soda solution are heated in iron pans to about 250° in a current of air, cooled and the fused mass extracted with water. This contains sodium oxalate. With lime, insoluble calcium oxalate is precipitated, which, with dilute H_2SO_4, gives oxalic acid.

A recent process is to pass carbon monoxide under pressure into caustic soda whereby sodium formate is produced. When this is *rapidly* heated to a fairly high temperature, sodium oxalate results (p. 77). The free acid is liberated with dilute H_2SO_4 from the insoluble calcium salt as usual.

$$NaOH + CO = \underset{\text{Sodium formate}}{HCOONa}.$$

$$\underset{\text{Sodium formate}}{2HCOONa} = \underset{\text{Sodium oxalate}}{NaOOC.COONa} + H_2.$$

Ethylene glycol, $HOH_2C\text{-}CH_2OH$, on oxidation, yields oxalic acid just as ethyl alcohol gives acetic acid (p. 77).

Properties.—Oxalic acid forms large, colourless prisms with two mols. of water; by careful heating to 100°, the anhydrous acid may be obtained, which melts at 189°, is soluble in water and alcohol but sparingly soluble in ether. Oxalic acid and its salts are poisons.

Dehydrating agents such as H_2SO_4 breaks up oxalic acid, on warming, as follows:

$$HOOC.COOH = CO_2 + CO + H_2O.$$

The acid is readily and *quantitatively* oxidised by potassium permanganate solution containing H_2SO_4 on warming to 60°.

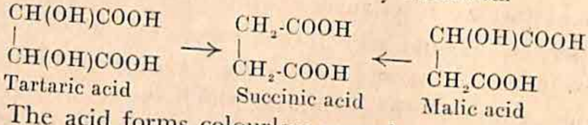
$$2KMnO_4 + 3H_2SO_4 + \underset{\text{Oxalic acid}}{5C_2H_2O_4} = 10CO_2 + 8H_2O + K_2SO_4 + 2MnSO_4.$$

This reaction is utilised in estimating the acid. As usual, it forms acid and neutral salts *e.g.*, HOOC.COOK and KOOC.COOK as well as acid and normal esters with alcohols. It forms, with PCl_5, oxalyl chloride, ClOC.CO.Cl, but *no anhydride is known.* Heated with glycerol, oxalic acid splits up into formic acid and CO_2 (p. 75).

$$\underset{\text{Oxalic acid}}{HOOC.COOH} = \underset{\text{Formic acid}}{HCOOH} + CO_2.$$

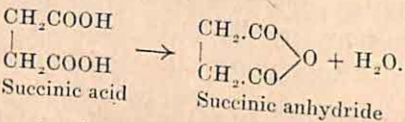
Uses.—Oxalic acid is widely used as a mordant in dyeing, cloth printing and also in cleaning leather. The acid is an ingradient of most metal polishes. Potassium quadroxalate or 'salt of sorrel' is used in removing ink-stains and iron-moulds from cloth and also in bleaching straw for hats. Potassium ferrous oxalate, $K_2Fe(C_2O_4)_2,H_2O$, is a developer in photography.

Succinic acid, $HOOC.CH_2.CH_2.COOH$, was originally obtained by the dry-distillation of amber (*succinum*), hence the name. Some succinic acid is even now made likewise. Tartrates or malates, on fermentation with yeast, yield succinic acid. This is commercially followed.



$$\underset{\text{Tartaric acid}}{\begin{array}{l} CH(OH)COOH \\ | \\ CH(OH)COOH \end{array}} \rightarrow \underset{\text{Succinic acid}}{\begin{array}{l} CH_2\text{-}COOH \\ | \\ CH_2\text{-}COOH \end{array}} \leftarrow \underset{\text{Malic acid}}{\begin{array}{l} CH(OH)COOH \\ | \\ CH_2COOH \end{array}}$$

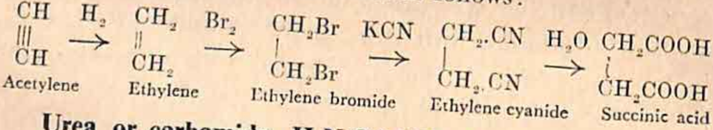
The acid forms colourless crystals (m.p. 185°), soluble in water. It is a very weak acid. On heating, succinic acid forms the anhydride:



$$\underset{\text{Succinic acid}}{\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}} \rightarrow \underset{\text{Succinic anhydride}}{\begin{array}{l} CH_2.CO \\ | \\ CH_2.CO \end{array}} \!\!>\! O + H_2O.$$

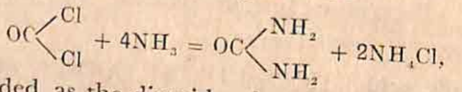
Boiled with water, the anhydride gives back the acid. Potassium succinate solution, on electrolysis, gives ethylene (*cf.* ethane, p. 30). The acid is sometimes used in standardising alkalis in the laboratory, and its anhydride in making some dyes.

Acetylene gives succinic acid as follows:



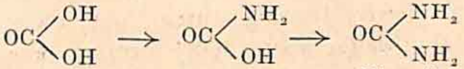
$$\underset{\text{Acetylene}}{\begin{array}{l} CH \\ ||| \\ CH \end{array}} \xrightarrow{H_2} \underset{\text{Ethylene}}{\begin{array}{l} CH_2 \\ || \\ CH_2 \end{array}} \xrightarrow{Br_2} \underset{\text{Ethylene bromide}}{\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array}} \xrightarrow{KCN} \underset{\text{Ethylene cyanide}}{\begin{array}{l} CH_2.CN \\ | \\ CH_2.CN \end{array}} \xrightarrow{H_2O} \underset{\text{Succinic acid}}{\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}}$$

Urea or carbamide, $H_2N.CO.NH_2$, has some historical importance as it was the first organic compound to be synthesised in the laboratory (p. 1), but its presence in the urine of mammals was known much earlier, whence the name. An adult passes about 30 g. of it per day. Urea comes from the protein food we take. Since carbonyl chloride, $COCl_2$, and ammonia give urea



$$OC\!\left\langle\begin{array}{l} Cl \\ Cl \end{array}\right. + 4NH_3 = OC\!\left\langle\begin{array}{l} NH_2 \\ NH_2 \end{array}\right. + 2NH_4Cl,$$

it was regarded as the diamide of carbonic acid:



Carbonic acid Mono-amide (carbamic acid) Di-amide (carbamide or urea)

But the present-day view about its structure is somewhat complicated.

Preparation.—(*i*) On adding nitric acid to a highly concentrated urine, urea nitrate, $CO(NH_2)_2.HNO_3$, separates. Barium carbonate liberates urea from the nitrate. Urea is extracted from the mass with alcohol which is then evaporated off.

(*ii*) An aqueous solution of ammonium cyanate (or a mixture of pot. cyanate and ammon. sulphate) on evaporation on water-bath, gives urea (and pot. sulphate). Alcohol extracts the urea but not the sulphate. This is how Wöhler obtained it:

$$\underset{\text{Ammon. cyanate}}{NH_4.CNO} \Longleftrightarrow \underset{\text{Urea}}{CO(NH_2)_2}$$

(*iii*) In the commercial method, ammonia and CO_2 with a little moisture are passed into an autoclave at about 140°. Ammonium carbamate, first formed, splits up into urea and water.

$$2NH_3 + CO_2 \dashrightarrow \underset{\text{Ammon. carbamate}}{H_2N.CO.ONH_4} \longrightarrow \underset{\text{Urea}}{H_2N.CO.NH_2} + H_2O.$$

Properties.—Urea is a colourless, odourless, crystalline solid (m.p. 132°), readily soluble in alcohol and water, but insoluble in ether. The aqueous solution is neutral to litmus. But urea behaves as a feeble *mono*-acidic base, forming with HNO_3 urea nitrate, $H_2N.CO.NH_2.HNO_3$, which is sparingly soluble in dilute HNO_3.

The oxalate, $CO(NH_2)_2.H_2C_2O_4$, is insoluble in water and useful in the detection of urea.

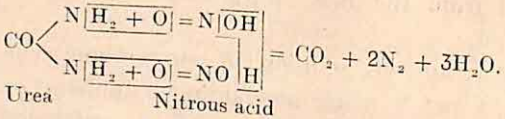
Reactions.—(*i*) Like other amides, urea liberates ammonia on hydrolysis with boiling NaOH.

$$H_2N.CO.NH_2 + 2NaOH = Na_2CO_3 + 2NH_3.$$

(*ii*) On slowly heating, urea first melts and then suddenly solidifies (at about 160°) forming biuret and NH_3. Its aqueous solution turns red-violet with NaOH and dilute copper sulphate solution. Urea may be detected by this test.

$$H_2N\text{-}CO\text{-}NH\underset{\text{Urea}}{\boxed{H + H_2N}}\text{-}CO\text{-}NH_2 = \underset{\text{Bi-uret}}{H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH_2} + NH_3.$$

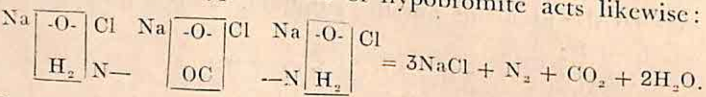
(*iii*) Nitrous acid oxidises urea to CO_2, N_2 and water (*cf.* methylamine, p. 96).



$$CO\begin{cases} N\boxed{H_2 + O} = N\boxed{OH} \\ N\boxed{H_2 + O} = NO\ \boxed{H} \end{cases} = CO_2 + 2N_2 + 3H_2O.$$

Urea Nitrous acid

(*iv*) Sodium hypochlorite or hypobromite acts likewise:



$$\begin{array}{llll} Na\,\boxed{\text{-O-}}\,Cl & Na\,\boxed{\text{-O-}}\,Cl & Na\,\boxed{\text{-O-}}\,Cl & \\ \boxed{H_2}\,N\text{—} & \boxed{OC} & \text{—}N\,\boxed{H_2} & = 3NaCl + N_2 + CO_2 + 2H_2O. \end{array}$$

By absorbing the CO_2 with conc. KOH solution in a nitrometer, the nitrogen evolved is measured. Urea in urine is thus roughly estimated.

Uses.—By far the most important use of urea to-day is in the manufacture of synthetic plastics with formaldehyde. Such plastics are used for too many purposes ; one interesting application is in producing anti-crease effect in cotton fabrics. Urea is also a fertiliser, it supplies nitrogen to the soil. Urea stibamine is a valuable remedy for Kala-azar.

Uric acid, $C_5H_4O_3N_4$, is a complex derivative of urea, and occurs with it in urine ; we pass about a gram of its acid ammonium salt per day. Its accumulation in our joints produces gout and rheumatism ; stones may be formed in different parts of our body by its deposition. Gouty people have much of it in their blood as well. White spots on the wings of butterflies are of uric acid. Excreta of birds and reptiles contain much uric acid. Excreta of serpents represent almost pure ammonium urate. Monkeys excrete much less uric acid than men.

Excrement of snakes or birds (guano) is boiled with NaOH; sodium urate formed is then acidified with HCl. On cooling, uric acid separates. The crystals have peculiar shapes and can be readily recognised under the microscope (Fig. 46).

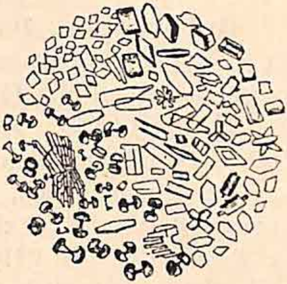
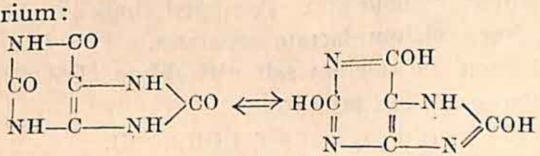


Fig. 46. Crystals of uric acid.

Properties.—Uric acid is a white crystalline powder, very sparingly soluble in water and insoluble in alcohol and ether. It dissolves in glycerol, strong H_2SO_4 and sodium carbonate solution. On heating, it decomposes into ammonia, urea, etc. It behaves as a weak, dibasic acid though it contains no carboxyl group, the hydrogens of the -NH- groups are acidic and replaced by metals. Lithium urate is fairly soluble in water; so gouty patients are sometimes given lithia-water. Uric acid exists in two forms in equilibrium:



Uric acid

Questions

1. How is oxalic acid made commercially? State its properties and chief uses.

2. How can succinic acid be synthesised from elements? Give essential details.

3. Why urea is called carbamide? How can you obtain it from urine? What happens when urea is heated?

4. Write down the structural formula for uric acid, urea, succinic anhydride, and carbamic acid.

CHAPTER XV

Hydroxy-acids.—If a hydrogen atom of the alkyl radical in a fatty acid be replaced by a hydroxyl group, $-OH$, we get a hydroxy-acid. Hydroxy-acetic acid or glycollic acid is $CH_2(OH).COOH$. Ethylene glycol, on oxidation under suitable condition, yields glycollic aldehyde (p. 58) which on further oxidation, gives glycollic acid. The most important member of this family is hydroxy-propionic acid or lactic acid, $CH_3.CH(OH).COOH$, which occurs in sour milk (Latin *lac*, milk). Scheele, a Swedish apothecary, first isolated it from sour milk in 1780.

Lactic acid, $CH_3CH(OH)COOH$, occurs also in gastric juice, opium and cucumbers. Lactose or milk-sugar of milk is fermented to lactic acid when milk turns sour:

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Lactic acid}}{4CH_3CH(OH)COOH}.$$

The acid is made from cane-sugar, glucose or starch, and also from molasses from sugar factories. Starch is first hydrolysed to simpler sugar. The ferment, *lactic bacilli*, in the form of sour milk or decaying cheese is added to the sugar solution at about 40°. Powdered chalk is added from time to time, calcium lactate separates. The free acid is obtained from the calcium salt with dilute H_2SO_4 followed by distillation at low pressure.

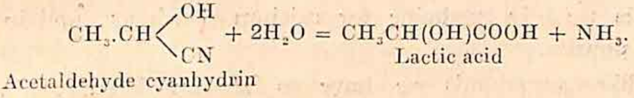
$$\underset{\text{Glucose}}{C_6H_{12}O_6} = \underset{\text{Lactic acid}}{2CH_3CH(OH)COOH}.$$

Lactic acid may also be prepared by hydrolysing alpha-chloro-propionic acid or treating it with *moist* silver oxide:

$$\underset{\alpha\text{-Chloro-propionic acid}}{CH_3.CHCl.COOH} + H_2O = \underset{\text{Lactic acid}}{CH_3CH(OH)COOH} + HCl.$$

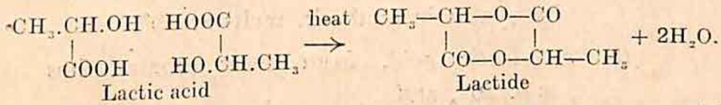
$$CH_3CHClCOOH + AgOH = CH_3CH(OH)COOH + AgCl.$$

Acetaldehyde cyanhydrin, on hydrolysis, gives lactic acid.



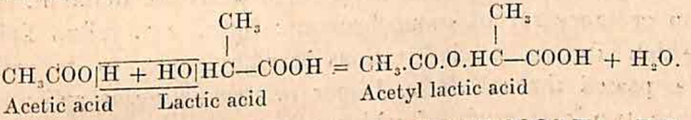
$$\underset{\text{Acetaldehyde cyanhydrin}}{\mathrm{CH_3.CH}\!\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{CN}\end{matrix}\right.} + 2H_2O = \underset{\text{Lactic acid}}{CH_3CH(OH)COOH} + NH_3.$$

Properties.—Lactic acid is a colourless, thick, hygroscopic liquid which decomposes on heating under ordinary pressure. It mixes with alcohol, ether and water in any proportion, and forms insoluble calcium and zinc salts. Heated alone, it forms, amongst others, a cyclic di-ester, called *lactide* (so the acid cannot be dehydrated by heating):



$$\underset{\text{Lactic acid}}{\begin{array}{ll}\mathrm{CH_3.CH.OH} & \mathrm{HOOC}\\ \mid & \quad\mid \\ \mathrm{COOH} & \mathrm{HO.CH.CH_3}\end{array}} \xrightarrow{\text{heat}} \underset{\text{Lactide}}{\begin{array}{l}\text{CH}_3\text{—CH—O—CO}\\ \qquad\mid \qquad\qquad \mid\\ \text{CO—O—CH—CH}_3\end{array}} + 2H_2O.$$

Lactic acid behaves both as an alcohol and as an acid, having two functional groups, —OH, and —COOH, in the molecule. Thus it reacts with an acid (as an alcohol) and also with an alcohol (as an acid):



$$\underset{\text{Acetic acid}}{\mathrm{CH_3COO}}\overline{\underline{\mathrm{H + HO}}}\underset{\text{Lactic acid}}{\overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\mathrm{HC}}}\text{—COOH}} = \underset{\text{Acetyl lactic acid}}{\mathrm{CH_3.CO.O.}\overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\mathrm{HC}}}\text{—COOH}} + H_2O.$$

$$\underset{\text{Lactic acid}}{\mathrm{CH_3.CH(OH)COO}}\overline{\mathrm{H + HO}}\underset{\text{Ethyl alcohol}}{\mathrm{C_2H_5}} = \underset{\text{Ethyl lactate}}{\mathrm{CH_3CH(OH)COOC_2H_5}} + H_2O.$$

Heated with dilute H_2SO_4, it gives acetaldehyde and formic acid:

$$\underset{\text{Lactic acid}}{CH_3CH(OH)COOH} = \underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Formic acid}}{HCOOH}.$$

On oxidation, it yields pyruvic acid, the secondary alcoholic group being converted into a ketonic group:

$$\underset{\text{Lactic acid}}{CH_3CH(OH)COOH} + O = \underset{\text{Pyruvic acid}}{CH_3.CO.COOH} + H_2O.$$

Uses.—Lactic acid is widely used in dyeing and tanning, antimony lactate in dyeing wool and also in calico printing, and the free acid for removing lime from hide. Ethyl lactate is a good solvent for lacquer varnish. Calcium lactate is used in medicine for calcium deficiency, and in baking powder.

Unlike compounds we have so far considered, lactic acid has a special property ; it exists in *three* isomeric forms, all being α-hydroxy-propionic acid, $CH_3CH(OH)COOH$, *i.e.*, they do not apparently differ in structure or constitution. These possess *identical* chemical properties but have somewhat different physical characters, *viz.*,

(*a*) *Ordinary lactic acid*, obtained from sour milk or by synthetic methods, melts at 18°,

(*b*) *Sarco-lactic acid*, from meat extract, has a m.p. 26°, and

(*c*) *Lactic acid that does not occur in nature* but is prepared from the ordinary acid by special methods, has a m.p. 26°.

Optical properties of these three acids are different. If an ordinary ray of monochromatic light, *e.g.*, yellow light which vibrates in all directions at right angles to its path, be passed through Iceland spar or tourmaline, it splits up into two rays, each of which vibrates in *one* plane only. Such rays are said to be polarised, they have different refractive indices. Consequently, by combining two prisms of Iceland spar, suitably cut, it is possible to have total internal reflection for one of the rays and allow the other to pass on. This combination of prisms is called a *Nicol prism*. If a second prism be placed in the path of the transmitted polarised ray, with its axis parallel to that of the first, the polarised ray will pass through with full intensity. But if it be rotated through 90°, the polarised ray is completely cut off.

Now, with the two Nicol prisms in the same axial line, the polarised ray passes all right. If we place some aqueous solution of sarco-lactic acid between these two, we have to rotate one of the prisms through a certain angle in order to get the light of original intensity. The liquid, therefore, has turned the plane of polarised light either to the right or to the left. This phenomenon is called *optical activity* and the substance is stated to be *optically active.* It is dextro- or lævo-rotatory according as it rotates the plane of polarised light to the right or left. This optical behaviour is associated with asymmetry of the molecule itself; this fundamental fact was discovered simultaneously by van't Hoff and Le Bel in 1874. Compounds that have four *different* groups or atoms attached to any one carbon atom, generally exhibit this property of turning the plane of polarised light either to the right or to the left. Thus, of the following, only lactic acid is optically active.

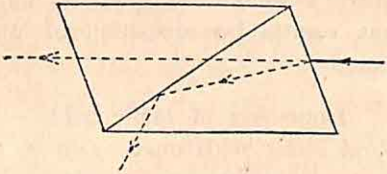
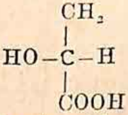
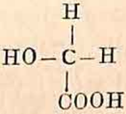


Fig. 33. Nicol prism.



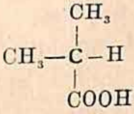
$$\begin{array}{c} CH_2 \\ | \\ HO-C-H \\ | \\ COOH \end{array}$$

Lactic acid



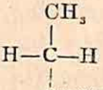
$$\begin{array}{c} H \\ | \\ HO-C-H \\ | \\ COOH \end{array}$$

Glycollic acid



$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-H \\ | \\ COOH \end{array}$$

Iso-butyric acid



$$\begin{array}{c} CH_3 \\ | \\ H-C-H \\ | \\ COOH \end{array}$$

Propionic acid

Carbon has the valency bonds not on the same plane but in different directions in space—it is believed to be at the centre of a regular tetrahedron while the valencies are directed

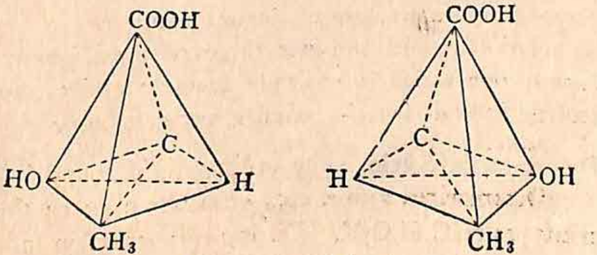


Fig. 34. Lactic acid molecules.

towards the four appexes. Thus represented, lactic acid will appear as shown in Fig. 34. It may be noted that one is the mirror image of the other like our right and left palms, and one *cannot* be superimposed upon the other to coincide exactly.

Isomerism of lactic acids.—We may now consider the three lactic acids once again in so far as their optical properties are concerned. The sour-milk acid has *no action* on polarised light, so it is optically inactive. Sarco-lactic or muscle acid turns the plane of polarised light to the right, hence it is dextro-rotatory (*d*-) and the third acid, derived from the sour-milk acid, rotates the plane to the left, it is, therefore, lævorotatory (*l*-). It may be noted that equal weights of the latter two, when mixed together, give an inactive combination which is the sour-milk lactic acid. The rotations of the two acids (*d*- and *l*-) are *exactly* equal but *opposite* in direction ; hence one nullifies the effect due to the other when present in *equal* amounts. There are methods for resolving an inactive product into its active components. Isomerism exhibited by the lactic acids is known as *optical isomerism.*

Tartaric acid, HOOC.CHOH.CHOH.COOH, a dihydroxy dicarboxylic acid, occurs in four isomeric forms: (*i*) Dextro-tartaric acid (*d*-), (*ii*) Lævo-tartaric acid (*l*-), (*iii*) Racemic tartaric acid (*dl*-) and (*iv*) Meso-tartaric acid.

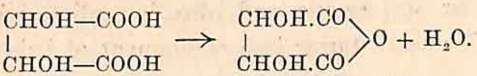
From our knowledge of lactic acid, we can see the optical relationship of the first three of these isomers but the fourth one which is optically inactive and cannot also be resolved into *d*- and *l*- varieties, presents some difficulty.

Dextro-tartaric acid is the ordinary acid found in many fruits *e.g.*, tamarind, grape, etc., either free or as the acid potassium salt, $C_4H_5O_6K$. During fermentation of grape juice to wine, this salt, being insoluble in aqueous alcohol, separates as a brown crust, called *argol,* wine-lees or tartar (recrystallised argol is called cream of tartar). The commercial source of the acid is argol from which Scheele first isolated it in 1769. Argol is dissolved in boiling water and nearly neutralised with chalk. Half the acid separates as the insoluble normal calcium salt, and removed by filtration; the other half remains in solution as neutral pot. tartrate. This is converted into normal calcium tartrate by adding calcium chloride solution. The free acid is liberated with H_2SO_4 as usual.

$$\underset{\text{Acid pot. tartrate}}{2KHC_4H_4O_6} + CaCO_3 = \underset{\text{Pot. tartrate}}{K_2C_4H_4O_6} + CO_2 + \underset{\text{Calcium tartrate}}{CaC_4H_4O_6} + H_2O.$$

$$CaCl_2 + \underset{\text{Pot. tartrate}}{K_2C_4H_4O_6} = 2KCl + \underset{\text{Calcium tartrate}}{CaC_4H_4O_6}$$

Properties.—*d*-Tartaric acid forms large, transparent prisms (m.p. 170°) which are anhydrous. The acid readily dissolves in water but not in ether. As a dibasic acid, it forms two series of salts and esters—acid and normal. It reduces silver nitrate to metallic silver from ammoniacal solution and is used in mirroring of glass. Heated to 150°, it forms the anhydride:



$$\begin{array}{l} CHOH{-}COOH \\ | \\ CHOH{-}COOH \end{array} \longrightarrow \left.\begin{array}{l} CHOH.CO \\ | \\ CHOH.CO \end{array}\right\rangle O + H_2O.$$

Tartaric acid Tartaric anhydride

Lævo-tartaric acid is identical with the dextro- in *all* chemical and most physical properties. It turns the plane of polarised light to the left and to the *same* extent as the *d*-variety; the crystals of the *l*-acid are somewhat different in shape. Lævo-tartaric acid is usually obtained from the inactive racemic acid by methods of resolution. Like *d*- and *l*- lactic acids, *d*- and *l*- tartaric acids, on mixing in aqueous solution in *equal* amounts, form the racemic acid.

Racemic or dl-tartaric acid (also called para-tartaric acid) occurs in grape juice (Latin *racemus* bunch of grapes). It forms rhombic crystals with two mols. of water, the anhydrous acid melts at 204°. Racemic acid is less soluble in water than *d*- or *l*- acid, as also its calcium salt. Synthetic tartaric acid is *always* inactive, it is either racemic acid or a mixture of racemic and meso-tartaric acid.

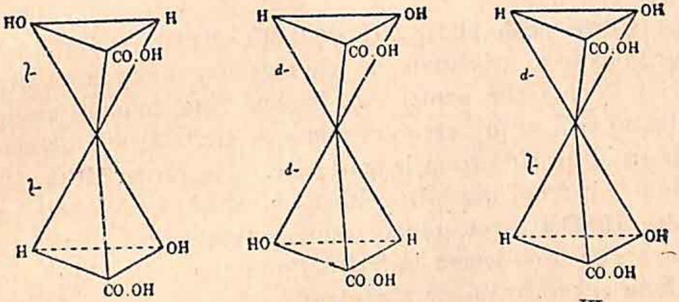
Meso-tartaric acid does not occur in nature. It may be obtained by heating *d*-tartaric acid with water to about 170° or with dilute acids. It crystallises with one mol. of water. Its potassium salt is more soluble in water but the calcium salt more insoluble than corresponding salts of tartaric (*d*- and *l*-) and racemic acids. It forms rectangular plates ; the anhydrous acid melts at 140°. Chemically, meso-tartaric acid is identical with other forms.

Uses.—Tartaric acid is extensively used in making saline drinks (*sherbet*) ; the sodium-potassium salt, commonly known as *Rochelle* salt, is used in making Fehling's solution, Seidlitz powder (a laxative) and also in mirroring of glass. Tartar emetic or potassium antimonyl tartrate is used in medicine as an emetic and also in calico printing and dyeing. Cream of tartar is a component of baking powder.

Isomerism of tartaric acids.—The tartaric acid molecule has *two* asymmetric carbon atoms, each of which has four *different* groups or atoms linked to it, *viz.*, -H, -OH, -COOH and -CH(OH).COOH. Since these groups and atoms are identical in both cases, it follows that the effect produced by them on polarised light will be the same in magnitude in respect of each carbon atom, the total effect of the molecule as a whole being additive. Four different cases may arise:

(*i*) Both the asymmetric carbon atoms cause the plane of polarisation to rotate clockwise *i.e.,* towards the right, giving dextro-tartaric acid (model II in Fig. 35).

(*ii*) Both may rotate the plane of polarisation in the opposite, *viz.,* counter-clockwise direction *i.e.,* to the left. The molecule will now appear to be a mirror image of the dextro-acid structurally, none has a plane of symmetry. It is the lævo-acid (Model I in Fig. 35).



I
l-Tartaric acid

II
d-Tartaric acid

III
i-Mesotartaric acid

Fig. 35

(*iii*) The groups may be so arranged in the molecule that one asymmetric carbon atom will turn the plane of polarised light to the right whilst the other will do so to the left. The net effect will be nil as one will annul the rotation due to the other (rotations being *equal* in magnitude but *opposite* in direction). This means that not only the compound will be inactive optically but also it will be incapable of resolution into *d*- and *l*- forms, as the compensation is internal over which we have no control. This is meso-tartaric acid (Model III in Fig. 35).

(*iv*) Lastly, we may have a combination of *equal* amounts of *d*- and *l*- acids ; the mixture will have no effect on polarised light inasmuch as half the number of molecules will turn the plane of polarised light to one direction whilst the remaining half will do so in opposite direction. Weights of each being equal, the magnitude of rotation will also be equal. We have racemic acid (like sour-milk lactic acid) which is externally compensated and so can be resolved into *d*- and *l*- forms as in the case of ordinary lactic acid.

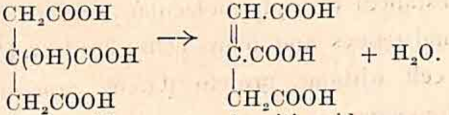
Pasteur, the famous French chemist, was the pioneer worker in this field of organic chemistry. You will read about his excellent researches later on.

Citric acid, $HOOCCH_2.C(OH)COOH.CH_2COOH$, is a mono-hydroxy tri-carboxylic acid that occurs free in all citrus fruits (hence the name) *e.g.*, lemon, lime, tomato, orange, etc., as well as in beet-root, potatoes, etc. Scheele obtained the acid in 1784 from lemon juice. He prepared the calcium salt from the juice with lime, which was decomposed with H_2SO_4. Even to-day large quantities of citric acid are made from lemon in Sicily, California and other places where citrus fruits are abundant.

Another commercial method is by fermentation of 10-12% solution of cane-sugar, glucose, etc. with certain moulds at about 40°. The yield of citric acid is nearly 50% of the weight of sugar used. In India it can be made from molasses of sugar factories.

Properties.—Citric acid is a white, crystalline solid containing a mol. of water of crystallisation. These crystals melt at 100° but the anhydrous acid melts at 153°. It is readily soluble in water and alcohol but insoluble in ether. The acid is optically inactive, having no asymmetric carbon atom in the molecule. Citrates do not reduce ammoniacal silver nitrate solution on warming; but on boiling, silver is slowly deposited. Unlike calcium tartrate, calcium citrate is soluble in cold but *insoluble* in boiling water. Hence citric acid can be distinguished from tartaric acid.

On heating up to 175°, citric acid loses a mol. of water and forms *aconitic acid* which is unsaturated:



$$\begin{array}{l} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array} \longrightarrow \begin{array}{l} CH.COOH \\ \| \\ C.COOH \\ | \\ CH_2COOH \end{array} + H_2O.$$

Citric acid Aconitic acid

Uses.—Citric acid is used in making lemonades, as a mordant in dyeing (mordants are compounds that help the fixation of dyes on fabrics) and in calico printing. Ferric ammon. citrate, magnesium citrate and sodium or potassium citrate are used in medicine.

Questions

1. How is lactic acid manufactured? State its important properties and uses.

2. How many tartaric acids are known? How is their isomerism explained?

3. What is optical activity? How are sour-milk lactic acid and muscle lactic acid related?

4. Write down the structural formula of citric acid and state how it is made. What are its chief uses?

5. What happens when (a) lactic acid is heated with dilute H_2SO_4, (b) dextro- and laevo- tartaric acid are mixed together in equal amount in water, and (c) citric acid is heated to 175°.

CHAPTER XVI

Proteins are a large group of complex, nitrogenous, organic substances of high molecular weights. They occur in all animal tissues and plant cells; in fact, there can be no living cell without protein (Greek *proteios,* primary). Some of the enzymes, vitamins, hormones and viruses have been shown to be proteins. They are mostly colloids but a few have been obtained crystalline. More than fifty proteins have so far been studied but few completely. Animals contain more proteins than plants in which cellulose predominates. The dry material in most animals consists almost wholly of proteins except some mineral matter, fats and carbohydrates. The average human body contains about 15% by weight of protein, nearly 65% being water. Animals can live without fats and carbohydrates for a considerable period but not without protein. Plants can build up their protein from inorganic sources but not animals who depend largely on plants for their protein supply. Unlike plants, animals rarely store protein, except in the form of living tissues. Vegetable proteins undergo some changes during assimilation by animals. We cannot, of course, assimilate all proteins equally. Good many proteins, *e.g.*, horn, hair, wool, silk, etc. are not foods. To the 3000 calories of heat, an average human being needs per day, very little, however, is supplied by proteins, their main function being to provide for the growth of new tissues and repair of the working parts. In plants, protein may occur as solid or in solution in the cell sap. Proteins are less commonly known as *albuminoids*. The protein contents of some common foodstuffs are given below.

Source	*Approx. protein %*	*Source*	*Approx. protein %*
Cow's milk ...	... 3	Cheese ...	... 33
Rice ...	... 8	Eggwhite ...	... 12·5
Peas ...	... 21	Raw potatoes ...	... 2
Egg yolk ...	... 16	White bread ...	... 6·5
Maize ...	... 9·9	Bananas ...	... 1·5
Cooked fowl ...	... 24	Wheat ...	... 14
Cooked beef ...	... 26	Ground nut ...	... 29

Composition.—In physical, chemical and physiological properties, proteins differ widely. But their elementary composition is more or less the same. Besides carbon, hydrogen and oxygen, they contain nitrogen and sulphur, and sometimes phosphorus, iron, copper or iodine. They invariably contain some mineral matter which gives ash on ignition. The average composition of proteins may be given as C—50-55%, H—6·5-7·3%, O—19-24%, N—15-19% and S—0·3-2·4%.

As already pointed out, the building stones of the gigantic protein molecules are the amino-acids (p. 93). They consist of indefinite chains of amino-acids, united by linkages of the type —CO.NH—, the -COOH group of one amino-acid being joined to the amino group, $—NH_2$, of another, with the elimination of water. Two mols. of amino-acetic acid or glycine, $H_2N.CH_2.COOH$, thus combine to give glycyl-glycine, $H_2N.CH_2.CO.NH.CH_2.COOH$, a *dipeptide*. Peptides of high mol. wt., resulting from the combination of many amino-acids in a like manner, are called *polypeptides*. On hydrolysis, therefore, proteins yield α-amino-acids, *i.e.*, acids containing the amino group, $-NH_2$, attached to the carbon next to the carboxyl group, -COOH. Some 25 amino-acids have so far been isolated from proteins. They are all optically active.

Egg albumin (the white of egg) belongs to the group of albumins which are neutral bodies, readily soluble in water and dilute salt solutions but are easily coagulated by heat. Once coagulated, they do not dissolve in water but dissolve in acids and alkalis. They can be obtained in crystalline form. Such proteins can be 'salted out' with saturated ammon. sulphate solution from their aqueous solutions. The mol. wt. of egg albumin has been found to be about 34,000. Plants synthesise vegetable albumins from inorganic sources.

Casein, a protein of milk, contains phosphoric acid units in its molecular chain (P=0·8%). It is insoluble in water ; due to acidic nature, it is soluble in alkali. From the alkaline solution it is precipitated by acids. Casein is used in making invalid food, in the manufacture of plastics (*galalith*) with formaldehyde, in sizing paper so that ink does not run, and in making casein glue. 'Lanital' is an artificial wool discovered in Italy in 1936 ; this is made from casein of milk. Cheese contains casein. The mol. wt. of casein has been calculated as 16,000.

Gelatine forms an insoluble compound with tannins ; this is commercially utilised in the tanning of hide into leather. Dried baker's yeast may contain more than 45% of protein. This can be processed to a meat-like product which has been used as a protein diet. Compressed yeast is now made economically. *Marmite* is an extract of yeast.

Fats supply much more energy than proteins or carbohydrates (see next chapter). One lb. of fat yields 4000 kilogram calories while 1 lb. of protein gives only 1800 which is also obtained from a lb. of carbohydrate.

Reactions of proteins.—(*i*) All proteins give the biuret reaction (p. 108). On adding a few drops of a *very dilute* solution of $CuSO_4$ to a solution of protein, made alkaline with an excess of NaOH solution, a red-violet colour appears.

(*ii*) A protein solution, on warming with a little conc H_2SO_4, turns yellow. The colour changes to orange with excess of ammonia. This is known as xanthoproteic (Greek *xanthos* yellow) reaction.

(*iii*) When an alcoholic solution of α-naphthol and then conc. H_2SO_4 are added to a protein solution, a violet colour is formed at the junction of the two liquids (*Molish's reaction*).

(*iv*) Proteins containing albumin coagulate on heating their solution with acetic acid; those containing sulphur, turn black on boiling their solution with NaOH and lead acetate solution due to the formation of PbS.

Questions

1. What are proteins? Why are they so called? Name some common proteins you know.

2. What are the building units of proteins and how are they linked? Name the elements that occur in proteins, with the approximate percentage.

3. Name some common foods that are rich in proteins. Give some instances of industrial applications of proteins.

CHAPTER XVII

Carbohydrates.—We are quite familiar with cane-sugar, rice, wheat, maize, etc., which chemists call *carbohydrates.* Our daily food consists of three main types, *viz.,* proteins, carbohydrates and fats. In India, starchy foods *i.e.,* carbohydrates form the largest proportion. Carbohydrates are, therefore, important. They are important also because another essential article of daily life, *viz.* clothing, is made mainly of cotton which consists principally of cellulose, another carbohydrate. Paper is cellulose in impure form, and may be called a carbohydrate. Artificial silk or rayon, celluloid, cellophane, cinema films, gun-cotton, etc. are all derived from carbohydrates.

The general formula for this class of compounds may be expressed as $C_x(H_2O)_y$ as they consist of C, H and O, and the latter two in the proportion in which they occur in water. Hence they are called carbohydrates, but this is not literally correct as all sugars cannot be expressed likewise and there are compounds such as formaldehyde, CH_2O ; lactic acid, $C_3H_6O_3$; acetic acid, $C_2H_4O_2$, etc. that have formulæ like carbohydrates but are *not* carbohydrates. The name, however, has been retained for want of a more suitable one. Carbohydrates are classified under three main groups:

(*i*) Sugars e.g., cane-sugar, glucose, milk-sugar, etc.
(*ii*) Starches, such as rice, wheat, potato, barley, etc.
(*iii*) Celluloses, in the form of cotton, straw, jute, wood, bamboo, grass, etc.

Sugars are further classified according to their molecular composition ; *monosaccharides* are sugars containing up to 9 C-atoms, *e.g.* xylose, a pentose, $C_5H_{10}O_5$; glucose, a hexose, $C_6H_{12}O_6$, etc. *Disaccharides* have 12 C-atoms, *e.g.* cane-sugar, $C_{12}H_{22}O_{11}$. *Polysaccharides* contain more C-atoms, e.g. starch, $(C_6H_{10}O_5)n$.

Glucose, $C_6H_{12}O_6$, is a well-known invalid food. It occurs widely in the nectar of flowers, seeds and leaves of plants. The name is due to its sweet taste (Greek *glucus*, sweet). Ripe grapes contain 20-30% of it; hence the name grape-sugar. Honey is a mixture of glucose and fructose (1:1) in water (20%). Cane-sugar consists of glucose and fructose; on hydrolysis with dilute mineral acids, it splits as

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}.$$

A very large number of glucose units make starch and cellulose. Hence, on hydrolysis, both starch and cellulose yield glucose finally. One can, therefore, make glucose from a cotton cloth, a wooden table or rice straw. Such glucose is reported to be converted into alcohol by fermentation in Soviet Russia. *Glucosides* are compounds of glucose and other substances; *amygdalin* (p. 100) is a glucoside. *Anthocyanins*, the water-soluble colouring matters of plants and flowers, are also glucosides. Some tannins are esters of glucose and aromatic acids. *Indican*, a glucoside of indigo plant, gives indigo on hydrolysis and oxidation.

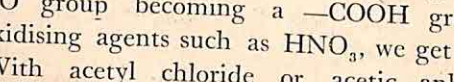
Glucose in traces (about 0·1%) occurs in our blood and also in urine; but diabetic patients, having a defective digestive system, cannot decompose starch beyond the glucose stage and pass large amounts of it (about 10% sometimes) with urine.

In the laboratory, glucose may be made from cane-sugar by warming with strong HCl in alcohol. Fructose, being more soluble than glucose in alcohol, remains in solution while glucose comes out as crystals on adding a few glucose crystals to induce crystallisation.

Glucose is manufactured by hydrolysing starchy materials like rice, maize or potato with dilute H_2SO_4 under pressure. The acid is neutralised with soda ash, filtered and concentrated.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O = \underset{\text{Glucose}}{nC_6H_{12}O_6}.$$

Properties.—Glucose is a white, crystalline solid, highly soluble in water. It crystallises with one mol. of water; this melts at 86°; from alcohol, anhydrous crystals appear, which melt at 146°. Glucose is dextro-rotatory, hence called *dextrose*. It reduces Fehling's solution and ammoniacal solution of silver nitrate like aldehydes (p. 69). The glucose molecule has five alcoholic —OH groups and one aldehyde group, —CHO. Its reactions with HCN, hydrazine, phenylhydrazine, hydroxylamine, etc. are similar to those of acetaldehyde (pp. 67-69). With phenylhydrazine, however, it reacts further, and finally gives phenyl glucosazone (m.p. 205°) which is characteristic of glucose (and also of fructose). Glucose may be written as $CH_2OH.CHOH.CHOH.CHOH.CHOH.CHO$ but the aldehyde group in glucose is not free, it forms a ring and glucose really is



$$\underbrace{HOH_2C.CH.CHOH.CHOH.CHOH.CHOH}_{\text{O}}$$

Since it has an aldehyde group, it is an *aldose*. On mild oxidation, *e.g.*, with bromine, glucose forms gluconic acid, the —CHO group becoming a —COOH group. With stronger oxidising agents such as HNO_3, we get oxalic acid finally. With acetyl chloride or acetic anhydride, all the five —OH groups may be acetylated to penta-acetyl glucose. Yeast converts glucose into alcohol and CO_2 (p. 53).

Uses.—Glucose is widely used in confectionery, in preserving fruits, making jams, silvering mirror and as food for the invalid. Calcium gluconate removes calcium deficiency. Ascorbic acid or vitamin C is a sugar derivative, one method for making it starts with glucose.

Fructose or fruit-sugar, $C_6H_{12}O_6$, occurs in the nectar of flowers, fruits and also in honey with glucose. Cane-sugar contains one mol. of glucose and one of fructose. Inulin, a plant product, is a polymer of fructose as cellulose is a polymer of glucose.

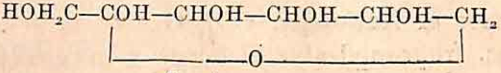
In the laboratory, fructose may be prepared by hydrolysing cane-sugar (*cf.* glucose) but to the neutralised solution containing glucose and fructose, slaked lime is added. Calcium fructosate, ($CaO.C_6H_{12}O_6$), being less soluble than calcium glucosate, separates out and is removed by filtration. Fructose is liberated from the aqueous suspension with CO_2.

Commercially, fructose is made from tubers of dahlia and Jerusalem artichoke which contain *inulin,* by hydrolysis with dilute H_2SO_4. The acid is removed with baryta and the solution of fructose concentrated under reduced pressure.

Properties.—From absolute alcohol, fructose forms rhombic crystals (m.p. 95°) but from water, it crystallises as $2C_6H_{12}O_6,H_2O$. It is lævo-rotatory, hence called *lævulose.* Like glucose, it is fermented by yeast to alcohol and CO_2 ; it gives the *same* osazone with phenylhydrazine (m.p. 205°) as does glucose. It has a ketone group, $>CO$; so fructose is a *ketose* as glucose is an *aldose*. It behaves like glucose towards most reagents ; one striking property of fructose is that it behaves as a strong reducing agent like an aldehyde—reducing Fehling's solution or ammoniacal silver nitrate solution—though it contains no aldehyde, —CHO, group. This is due to the *easy* oxidisability of the $CH_2OH.CO$- group in the molecule. Its formula may be written as

$$CH_2OH—CO—CHOH—CHOH—CHOH—CH_2OH,$$

but it has a ring structure which, however, opens up, like that of glucose, easily.



$$HOH_2C-\underbrace{COH-CHOH-CHOH-CHOH-CH_2}_{O}$$

Fructose

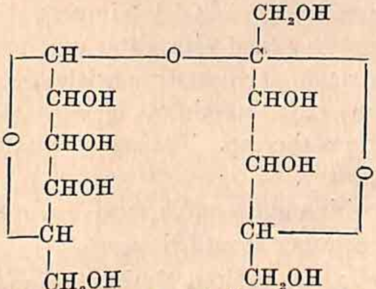
Diabetic patients cannot assimilate glucose which passes out with their urine ; they can, however, assimilate fructose. So they are given fructose instead of cane-sugar or glucose. Fructose is far more hygroscopic, *i.e.,* absorbs much more moisture from air, than glucose.

Cane-sugar, sucrose or saccharose, $C_{12}H_{22}O_{11}$, occurs in sugar-cane, sugar mapple, sorghum and beet. Beet-sugar and cane-sugar are identical. It is found in many fruits, e.g., pine-apple (11%), apricot (6%), ripe banana (5%), etc. In India cane-sugar was made and exported to Europe after Alexander's invasion in 327 B.C. Greek physicians used to call cane-sugar *Indian salt*. Sucrose was discovered in beet-root much later (in 1747) ; it originally contained only about 6% of sucrose but by research, it has been possible to raise this figure to about 28%. Sugar content of sugar-cane is about 12-13% in India but about 19% in Java. This is one of the reasons why India cannot produce cane-sugar as cheaply as Java.

Apparently, the process of sugar manufacture is simple ; the cane is cut into short pieces and passed through iron rollers ('crushing') to expel the juice that contains sugar. This juice is treated with lime and boiled to coagulate impurities ; through the solution is bubbled sulphur dioxide gas for decolorisation and removal of further impurities. The filtered solution is evaporated under reduced pressure to crystallisation. Sucrose crystallises much more readily than glucose or fructose. The crystals are separated from the brown, syrupy mother-liquor (molasses) by a centrifuge. Molasses serves as the raw material for alcohol, rum, cattle-food and fertiliser. Sugar candy is sucrose crystallised on threads, large aggregates are thus obtained.

There are some 160 sugar factories in India, mostly in U.P. and Bihar. We now produce about 10 lacs tons of sugar per year but our annual consumption is about 11·6 lacs tons. *Per capita* sugar consumption is 113 lb. in Australia, 103 lb. in U.S.A., 37 lb. in Europe, and only about 26 lb. in India including unrefined sugar *i.e.*, 'gur'.

Properties.—Sucrose is a colourless, crystalline solid, soluble in water but practically insoluble in alcohol. It is dextro-rotatory; pure sucrose melts at 188° and has no reducing property. On heating with a little water, sucrose melts and on cooling, forms a glassy mass known as *barley sugar*. At about 200°, it loses some water and gives *caramel*, a deep brown, soluble product, used extensively in confectionery. Boiling dilute acids, or certain enzymes hydrolyse it to equal amounts of glucose and fructose. The resulting solution is lævo-rotatory, the original optical rotation having been reversed; hence the mixture is called *invert sugar*. This is sweeter than sucrose and is used as food for the invalid and infants as well as a substitute for honey. Conc. HNO_3 oxidises sucrose to oxalic acid (p. 104). Yeast cannot directly ferment it to alcohol but *invertase*, present in most yeasts, converts it first into invert sugar which then undergoes alcoholic fermentation (p. 53). Sugar is an excellent energy-producing food, giving 1815 calories per lb. Cane-sugar is used in making transparent soaps. Sucrose syrup is a preservative in jams, etc.



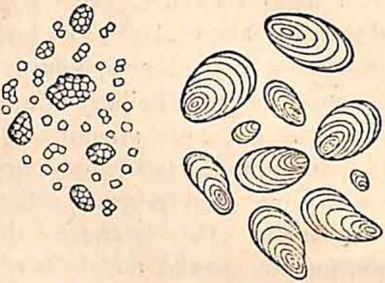
(Glucose residue) (γ-fructose residue)

Sucrose

Relative degrees of sweetness of common sugars :

Fructose	173	Malt sugar (maltose) ...	32
Invert sugar	130	Galactose	32
Sucrose	100	Milk-sugar (lactose) ...	16
Glucose	74	Saccharin	55,000

Starch or amylum, $(C_6H_{10}O_5)_n$.—Unlike the carbohydrates we have so far considered, starch is practically tasteless, insoluble in water and amorphous. As this and other complex carbohydrates such as cellulose consist of many, many simple sugar units, they are called *Polysaccharides*. Starch occurs in all green plants, specially in tubers, roots and seeds as a reserve food. Principal sources of starch are rice, maize, wheat, barley, corn, potato, sago, etc. Starch grains from different sources have different shape and size. The starch content of rice is about 75%, of wheat, 60-70%, of maize, 65-70%, of potato, 15-20%, and so on. *Cornflour* is a starch from maize.



Rice Potato

Fig. 37. Starch grains.

Manufacture of starch is fairly simple ; the grains are powdered, thoroughly mixed with water and passed through fine sieves which retain the coarser particles of plant tissues. On allowing it to settle, starch occupies the bottom layer, water is run off from the top. The starch may be dried and powdered, if necessary.

On heating with water, starch forms a colloidal solution (a concentrated solution is called *starch paste*) which gives a deep blue colour with iodine solution in potassium iodide. This colour disappears on heating but reappears on cooling.

Heated alone to about 200°, a gum-like, yellowish powder, *dextrin,* results from starch. It is soluble in cold water and used as a gum (*British gum*). The gloss that appears on ironing starched linen is due to dextrin formed. *Sago, arrowroot* and *tapioca* are starches, the first is obtained from the pith of certain palm stems and the other two from the tubers of some tropical plants.

Diastase, an enzyme, converts starch into maltose, $C_{12}H_{22}O_{11}$ (isomeric with cane-sugar), as does our saliva or the pancreatic juice. *Takadiastase* hydrolyses starch to glucose and is given to patients to help digestion of starchy food.

Uses.—Huge quantities of starch are converted into glucose, alcohol, adhesives, etc. It is extensively employed for sizing paper and finishing cotton fabrics. Starch is used in laundry and in making dusting powder.

Cellulose, $(C_6H_{10}O_5)_n$, is by far the most abundant organic substance found in nature. It has been calculated (very roughly, of course) that our earth contains a total of 1,100 billion kilograms of it, which is nearly half the weight of CO_2 present in the atmosphere. Plants build up cellulose from CO_2 and water which, in presence of light and chlorophyll, first form formaldehyde. This undergoes polymerisation giving starch, cellulose, etc. Cellulose is the main ingradient of the structural framework of plants. Cotton is almost pure cellulose; other plant products such as jute, flax, hemp, straw, wood, etc. contain cellulose associated with lignin, etc. These impurities are removed by chemical means and we get a moderately pure stuff which is not, however, pure cellulose as from cotton. Commercially, caustic soda under pressure, calcium sulphite, etc. are used for the removal of lignin. Filter paper is practically pure cellulose.

On hydrolysis with acids, cellulose gives only glucose. It is heavier than water (sp. gr. 1·58) and insoluble in most reagents. Cellulose is fairly resistant to caustic soda but not to acids. With 15-20% NaOH solution, under tension, flat, ribbon-like fibres of cotton swell up and become cylindrical and assume a silky lustre. This is popularly known as *mercerisation* after John Mercer, a pioneer worker in the field.

With nitric acid, under suitable conditions, cellulose trinitrate is obtained ; it is *gun-cotton,* the well known explosive. Gun-cotton, nitro-glycerine and vaseline together make *cordite,* the smokeless powder for the military. It is also a component of *blasting gelatine.* Collodion is a solution of cellulose dinitrate in alcohol and ether. *Celluloid* is made from the dinitrate of cellulose by heating to about 75° under pressure with camphor in alcoholic solution. It is a plastic used for making sundry materials. Rayon or artificial silk is made from cellulose or cellulose acetate by different processes. Cellulose acetate sheets form the 'unbreakable' glass of commerce. Paper is manufactured from cellulosic materials such as grass, bamboo, wood, etc. by digesting under pressure with NaOH solution. Lignin and some other constituents are thus removed and a pulp of cellulose obtained. This is bleached with sodium hypochlorite and obtained in the form of sheets after addition of *size* (rosin soap, alum, china clay, etc.). When unsized paper is passed through 80% H_2SO_4, we get *parchment paper,* a tough product. *Cellophane* or transparent paper is made by dissolving wood pulp in NaOH and carbon disulphide, CS_2, and forcing the viscous solution through a thin slot into an acid bath. It is a dust-proof wrapping material. Waterproofs are made from it by coating the surface with a transparent lacquer.

Questions

1. How is cane-sugar extracted from the juice of sugar cane? What is the action of conc. HNO_3, conc. H_2SO_4 and Fehling's solution on cane-sugar? I.Sc. 1953, E. Punjab Uni.

2. How is glucose made commercially? Write down its structural formula. What are its chief properties?

3. What is invert sugar? Why is it so called? How can you obtain fructose from invert sugar?

4. Write short notes on: celluloid, gun-cotton, mercerisation, polysaccharides, and dextrin.

CHAPTER XVIII

Aromatic hydrocarbons.—Plant products such as oil of bitter almonds, gum benzoin, balsam of Tolu, oil of winter-green, etc. were designated as *aromatic* on account of the pleasant smell or *aroma* they possess. With the progress of organic chemistry, it was discovered that they were all cyclic compounds and might be regarded as derived from the mother-substance, benzene, C_6H_6. Compounds derived from, or closely related to, benzene are now called aromatic (though many possess no aroma and others have a nauseous odour) to distinguish them from aliphatic compounds.

Aromatic compounds contain a higher percentage of C and a lower percentage of H than corresponding aliphatic compounds. Thus benzene, C_6H_6, has 92·3% carbon but hexane, C_6H_{14}, only 83·7%. In some respects aromatic compounds differ from the aliphatic, *e.g.*, H_2SO_4 sulphonates and HNO_3 nitrates aromatic compounds but not the aliphatic. It is, however, possible to transform some open-chain compounds into aromatic (and vice-versa) *e.g.*, acetylene may be converted into benzene (p. 40). The aromatic compounds outnumber the aliphatic, about 75% of organic compounds known belong to the aromatic group. Coal-tar is a common source of many of them—some 300 are reported therein. These can be converted into many other derivatives—also aromatic—thus the number multiplies. Dyestuffs are synthetic organic compounds and all are aromatic. In his rather childish effort to synthesise quinine (which has been possible only in 1944), an 18-year-old English youngman, W. H. Perkin, discovered accidentally in 1856 the first synthetic coal-tar dyestuff *mauve* in his private laboratory. This gave a strong impetus to explore the possibilities of coal-tar products which led to the development of aromatic chemistry. You will learn later on more about the fascinating story of how German chemists made artificial indigo, which resulted in *complete* suspension of the indigo cultivation in India.

Distillation of coal-tar.—When coal is strongly heated (to 1000°-1400°) in fire-clay or iron retorts, out of contact with air, we obtain:

(*i*) Coal-gas (about 17% of the coal taken)
(*ii*) Ammoniacal liquor (8-10%)
(*iii*) Coal-tar (4-5%) and
(*iv*) Coke (about 70%)

Coal-tar, a deep black, thick liquid with an unpleasant smell, was once a veritable nuisance but now supplies many valuable products. Its constituents are partially separated by re-distillation—the distillate being collected according to sp. gr. or temperature at which it comes:

	Temp. °C	sp. gr.	yield %
(*i*) Light oil or crude naphtha	up to 170°	0·92	7-8
(*ii*) Middle or carbolic oil ...	170-230°	1·01	8-10
(*iii*) Heavy or creosote oil ...	230-270°	1·04	8-10
(*iv*) Anthracene or green oil ...	270-360°	1·10	16-20
(*v*) Pitch	Left in still	1·3	50-60

These fractions are then individually worked for the separation of their constituents. The main constituents of these fractions are:

Light oil: Benzene, C_6H_6; toluene, $C_6H_5.CH_3$; xylenes, $C_6H_4(CH_3)_2$.

Middle oil: Carbolic acid or phenol, C_6H_5OH; naphthalene, $C_{10}H_8$.

Heavy oil: Cresols, $C_7H_7.OH$.

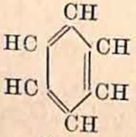
Anthracene oil: Anthracene, $C_{14}H_{10}$.

88
35

The light oil is re-distilled and the distillate below 70° rejected. The rest of the distillate contains about 65% benzene. This is treated with H_2SO_4 and then with NaOH solution to remove impurities, washed with water and again distilled with a fractionating column. The first portion is fractionated once more to get almost pure benzene. About 35 lb. benzene is obtained per ton of coal-tar.

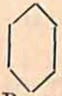
Benzene, benzol, C_6H_6, was discovered by Faraday, a world famous physicist, in 1825 in the illuminating gas made from whale oil. Hofmann detected it in coal-tar. (Benzene is a colourless liquid (b.p. 80·4°), lighter than water (sp. gr. 0·87) and insoluble in it. Solidified benzene melts at 5·4°. It is highly inflammable and burns with a smoky flame (*cf.* acetylene, p. 39). It has a characteristic but not unpleasant smell. Benzene is miscible with *dry* alcohol, ether, etc. It is a good solvent for phosphorus and iodine.)

It is a very stable compound though it has *three* double bonds ; it is resistant to permanganate and chromic acid. It forms hexa-hydrobenzene, C_6H_{12}, on catalytic hydrogenation, and benzene hexachloride, $C_6H_6Cl_6$, with chlorine in presence of sunlight. The stability is due to its peculiar balanced structure, having alternate single and double bonds. The establishment of the constitution of benzene has been a lengthy but interesting job which seems to be complete only recently. The constitution of benzene is



Benzene

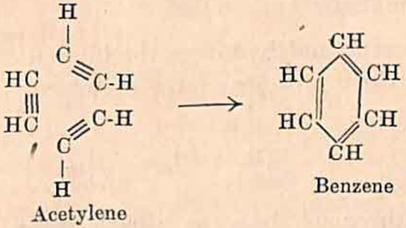
which is briefly written as



Benzene

Kekulé, a German chemist, hit upon this 'master design' for the benzene molecule in 1886 while travelling in an omnibus in the streets of London, almost in a day-dream. It has stood the test of time. Benzene may be obtained by synthetic methods but these are of academic interest only:

(i) Acetylene, on polymerisation, forms benzene (p. 40).



(ii) By distilling sodium benzoate, C_6H_5COONa, with soda-lime (*cf.* preparation of methane, p. 27):

$$C_6H_5COONa + NaOH = C_6H_6 + Na_2CO_3.$$

(iii) By distilling phenol, C_6H_5OH, with zinc dust:

$$C_6H_5OH + Zn = C_6H_6 + ZnO.$$

Reactions.—(1) In sun-light, benzene forms additive compounds with chlorine or bromine, 6 halogen atoms are thus finally added up. In presence of iron, I_2, etc., benzene yields substitution products, 6 hydrogen atoms are thus replaced by Cl_2 or Br_2.

$$\underset{\text{Benzene}}{C_6H_6} + 3Cl_2 = \underset{\text{Benzene hexachloride}}{C_6H_6Cl_6}$$ ✓

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow{Cl_2} \underset{\text{Chlorobenzene}}{C_6H_5Cl} \xrightarrow{Cl_2} \underset{\text{Dichlorobenzene}}{C_6H_4Cl_2} \xrightarrow{Cl_2} \underset{\text{Trichlorobenzene}}{C_6H_3Cl_3}, \text{ and so on.}$$

(2) In presence of H_2SO_4, benzene reacts with HNO_3, forming nitro-benzene; the water is taken up by H_2SO_4. At high temperature, dinitrobenzene, $C_6H_4(NO_2)_2$, results.

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O.$$

(3) Warm H_2SO_4 converts benzene into benzenesulphonic acid; fuming H_2SO_4 gives benzenedisulphonic acid, $C_6H_4(SO_3H)_2$.

$$\underset{\text{Benzene}}{C_6H_6} + H_2SO_4 = \underset{\text{Benzenesulphonic acid}}{C_6H_5SO_3H} + H_2O.$$

Reactions (2) and (3) distinguish aromatic hydrocarbons from the aliphatic.

✓(4) Benzene and hydrogen combine at 200° in presence of finely divided nickel to form cyclohexane or hexahydrobenzene.

$$\underset{\text{Benzene}}{C_6H_6} + 3H_2 = \underset{\text{Cyclohexane}}{C_6H_{12}}.$$

✓ (5) With ozone, benzene slowly forms a tri-ozonide, $C_6H_6O_9$, (*cf.* ethylene ozonide, p. 36):

$$C_6H_6 + 3O_3 = C_6H_6O_9.$$

Uses.—Benzene is used as a solvent for extracting fats and oils and also for dry washing. It is nitrated to nitrobenzene which is an important starting material for many compounds. Mixed with petrol, it is used as a motor fuel.

Toluene, $C_6H_5CH_3$, is the first homologue of benzene as ethane of methane, it is methyl-benzene. The monovalent radical, C_6H_5-, is known as *phenyl* as —CH_3 is called methyl. Toluene may as well be called phenylmethane, one hydrogen atom of methane, CH_4, having been replaced by a phenyl group, C_6H_5—. Toluene can be obtained by the dry distillation of *Tolu balsam*, whence the name. The main source of the hydrocarbon is, however, the light oil of coal-tar distillation; it also occurs in Assam and Borneo petroleum. About 5·5 lb. toluene is obtained per ton of coal-tar. The following methods are theoretically important:

(*i*) **Fittig's method.**—By reacting bromo- or iodo-benzene with methyl iodide and sodium in dry ether solution, toluene may be obtained:

$$\underset{\text{Bromobenzene}}{C_6H_5}\boxed{Br + 2Na + I}H_3C = \underset{\text{Toluene}}{C_6H_5{-}CH_3} + NaI + NaBr.$$

This is an extension of Wurtz synthesis of paraffins (p. 29).

(*ii*) **Friedel-Crafts' reaction.**—By treating an excess of benzene with a methyl halide in presence of anhydrous aluminium chloride:

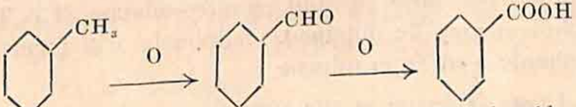
$$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl = \underset{\text{Toluene}}{C_6H_5CH_3} + HCl.$$

(*iii*) *n*-Heptane, $CH_3(CH_2)_5CH_3$, passed over chromic oxide at 500° gives toluene.

(*iv*) Toluene also results on distilling toluic acids, $C_6H_4(COOH)CH_3$, with soda-lime, or hydroxy-toluenes, $C_6H_4(OH)CH_3$, with zinc dust.

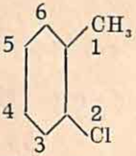
The methyl part of toluene is commonly called a *side-chain*. It may be noted, however, that a side-chain must contain one or more carbon atoms; thus phenol, $C_6H_5.OH$, has no side-chain.

Properties.—Toluene is a colourless liquid (b.p. 110°) lighter than water (sp. gr. 0·869) and closely resembling benzene in its behaviour. On oxidation, however, the methyl group is oxidised to a carboxyl group, —COOH, benzoic acid, C_6H_5COOH, being thus obtained. Any side-chain, however long, gives on oxidation a —COOH group. Mild oxidising agents *e.g.*, chromyl chloride, produce benz-aldehyde while chromic acid or $KMnO_4$, gives benzoic acid directly.

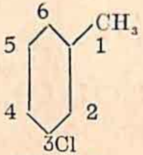


Toluene Benzaldehyde Benzoic acid

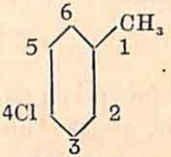
Chlorine may enter the benzene ring (*i.e.*, nucleus) or the side-chain, depending upon conditions. Thus, in the cold and in presence of iron, iodine, etc. chlorotoluene is formed, chlorine going to the nucleus. Three isomeric chloro-toluenes are known; the relative position of Cl with respect to the methyl group in the nucleus being different in each case. These are known as *ortho-*, *meta-*, and *para-*, briefly written as *o-*, *m-* and *p-* respectively.



o-Chlorotoluene



m-Chlorotoluene



p-Chlorotoluene

It may be noted that positions 1:2 and 1:6 are equivalent (called *ortho-*) as also position 1:3 and 1:5 (known as *meta-*). Thus of the 5 possible di-derivatives of toluene, only three are dis-similar.

If, however, chlorine is passed into *boiling* toluene, it goes to the side-chain, replacing one after another all the hydrogen atoms; three derivatives are thus formed:

benzyl chloride, $C_6H_5CH_2Cl$, (isomeric with chloro-toluene)

benzal chloride, $C_6H_5CHCl_2$, and

benzotrichloride, $C_6H_5CCl_3$.

These behave like alkyl halides, the Cl atom being replaceable by —OH, $—NH_2$ —CN, etc. groups (*vide* pp. 45-46).

Toluene is readily nitrated to mono-nitro-toluene; under suitable conditions, di- and tri-nitro-toluene (T.N.T. a high explosive) may be obtained. Sulphuric acid forms toluene-sulphonic acid from toluene.

Uses.—Toluene is the starting material for many dyes and drugs as well as T.N.T. It is a solvent and a motor fuel like benzene. Saccharin which is 550 times sweeter than cane-sugar, is made from toluene.

Aromatic halogen compounds.—Of the halogen derivatives of benzene, only the substitution products are important. The mono-halogen derivatives are

Chlorobenzene or phenyl chloride, C_6H_5Cl, (b.p. 132°)
Bromobenzene or phenyl bromide, C_6H_5Br, (b.p. 155°)
Iodobenzene or phenyl iodide, C_6H_5I, (b.p. 188°)

They are all colourless, heavy liquids, insoluble in water but soluble in alcohol and ether. They have a more or less pleasant smell. Both chloro- and bromo-benzene are made by passing dry chlorine, or adding bromine drop by drop, to benzene containing a little iron powder which acts as a catalyst, until theoretical increase in weight is attained, to avoid formation of di-halogen derivatives. Iodo-benzene may be made by heating in a sealed tube benzene, iodine and HNO_3.

$$\underset{\text{Benzene}}{6C_6H_6} + 3I_2 + 2HNO_3 = \underset{\text{Iodobenzene}}{6C_6H_5I} + 4H_2O + 2NO.$$

Chlorobenzene is mostly used in making synthetic phenol (carbolic acid), and D.D.T.

The halogen atoms in the benzene ring are firmly bound and cannot usually be replaced by —OH, —CN, —NH_2, etc. as in the case of ethyl iodide (pp. 45-46).

On chlorination, toluene should give *o*-, *m*- *and p*-chloro-toluenes but only the *o*- and *p*- derivatives are thus obtained. The *m*-compound is obtained by indirect methods. The chloro-toluenes, $C_6H_4(CH_3)Cl$, are colourless, heavy liquids with a pleasant smell. They resemble chloro-benzene. But when the chlorine enters the side-chain, we get three other derivatives (p. 140). Of these,

Benzyl chloride, $C_6H_5CH_2Cl$, is made by passing *dry* chlorine gas into boiling toluene until the required sp. gr. or increase in weight is reached. The reaction is accelerated by sunlight. Benzyl chloride (b.p. 179°) is separated from the unchanged toluene (b.p. 110°) by fractional distillation.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + Cl_2 = \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + HCl.$$

Benzyl chloride may as well be obtained by reacting benzyl alcohol with PCl_5:

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + PCl_5 = \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + HCl + POCl_3.$$

Benzyl chloride, $C_6H_5CH_2Cl$, is a colourless liquid, insoluble in water; it is isomeric with chloro-toluene, $C_6H_4(CH_3)Cl$, from which it can be distinguished by its pungent smell. Furthermore, benzyl chloride, unlike chloro-toluene, behaves like an alkyl halide:

$$\underset{\text{Benzyl chloride}}{2C_6H_5CH_2Cl} + K_2CO_3 + H_2O = \underset{\text{Benzyl alcohol}}{2C_6H_5.CH_2OH} + CO_2 + 2KCl.$$

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + NH_3 = \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} + HCl.$$

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + KCN = \underset{\text{Benzyl cyanide}}{C_6H_5CH_2CN} + KCl.$$

On oxidation with alkaline $KMnO_4$, benzyl chloride forms benzoic acid, $C_6H_5.COOH$, like toluene but chloro-toluenes form chloro-benzoic acids, $C_6H_4(Cl)COOH$. Here is another way of distinguishing between isomeric benzyl chloride and chloro-toluenes. Heated with copper or lead nitrate, benzyl chloride is oxidised to benzaldehyde, C_6H_5CHO.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + O = \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl.$$

The benzene ring in benzyl chloride may be nitrated with HNO_3 or sulphonated with H_2SO_4 in the same way as benzene itself, the $-CH_2Cl$ group remains intact. Benzyl chloride is chiefly used for making benzyl alcohol, $C_6H_5CH_2OH$.

Benzal chloride or benzylidene chloride, $C_6H_5CHCl_2$, is the next product of chlorination of toluene, two hydrogen atoms being replaced by chlorine. It may be prepared by the action of PCl_5 on benzaldehyde (*cf.* formation of ethylidene chloride from acetaldehyde, p. 68).

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + PCl_5 = \underset{\text{Benzal chloride}}{C_6H_5CHCl_2} + POCl_3.$$

But on a commercial scale, it is made by passing *dry* chlorine into *boiling* toluene until the required gain in weight is attained.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 2Cl_2 = \underset{\text{Benzal chloride}}{C_6H_5CHCl_2} + 2HCl.$$

Benzal chloride is a colourless liquid (b.p. 206°) with a pungent smell, provoking tears like benzyl chloride. Milk of lime hydrolyses it to benzaldehyde. This is how benzaldehyde, an important starting material for many dyes, is manufactured.

$$\underset{\text{Benzal chloride}}{C_6H_5CHCl_2} + Ca(OH)_2 = \underset{\text{Benzaldehyde}}{C_6H_5CHO} + CaCl_2 + H_2O.$$

Benzotrichloride, or phenylchloroform, $C_6H_5CCl_3$, is the final product of chlorination of toluene and is obtained by passing dry chlorine into boiling toluene until there is no more increase in weight.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 3Cl_2 = \underset{\text{Benzotrichloride}}{C_6H_5CCl_3} + 3HCl.$$

Benzotrichloride is a colourless liquid (b. p. 213°); on hydrolysis with milk of lime, or steam under pressure, it forms benzoic acid.

$$\underset{\text{Benzotrichloride}}{C_6H_5CCl_3} + 3H_2O = \underset{\text{Intermediate compound}}{C_6H_5C(OH)_3} + 3HCl$$

$$C_6H_5C(OH)_3 = \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O.$$

Questions

1. Describe the separation of benzene from coal-tar. How can benzene be converted into toluene and resorcinol?
I.Sc. 1952, Poona University.

2. Discuss the interaction between the following under different experimental conditions: (i) ethyl alcohol and conc. H_2SO_4, (ii) toluene and chlorine, and (iii) ethyl iodide and KOH.
I.Sc. 1954, Poona Uni.

3. Write short notes on: Fittig's method, Friedel-Crafts' reaction and hydrolysis.

4. What happens when (i) chlorine is passed into boiling toluene, (ii) benzyl chloride reacts with KCN, (iii) benzotrichloride is boiled with slaked lime, and (iv) benzyl chloride is treated with lead nitrate.

CHAPTER XIX

Nitro-benzene, $C_6H_5NO_2$, unlike nitro-paraffins, can be obtained by the direct nitration of benzene with HNO_3. This is one of the points of difference between aliphatic and aromatic compounds in general as already mentioned. For introducing the nitro group, $—NO_2$, to the benzene nucleus, usually a mixture of conc. HNO_3 (sp. gr. 1·4) and conc. H_2SO_4 is employed. The latter removes the water formed during the reaction and also prevents the dilution of the nitric acid. With dilute HNO_3, nitration is not generally possible except in some special cases.

$$\underset{\text{Benzene}}{C_6H_5}\boxed{H + \underset{\text{Nitric acid}}{HO}}-NO_2 = \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O.$$

This reaction is carried out in the cold. If the temperature is raised, or fuming HNO_3 be employed, we obtain di- or tri-nitro-benzene. This has to be avoided. In actual practice, a well-cooled mixture of conc. HNO_3 and H_2SO_4 is *gradually* added to cool benzene, with shaking and cooling if necessary, and the whole mass poured into a large volume of water. The heavy, oily nitro-benzene is drawn off from the bottom, washed with water, then with a dilute solution of soda ash, again washed with water, dried with fused $CaCl_2$ and distilled with an air condenser. The commercial method is also similar.

Properties.—Nitro-benzene is a pale yellow, oily liquid (b. p. 209°), heavier than water (sp. gr. 1·204) and insoluble in it. It smells like oil of bitter almonds and is used as a perfume. In commerce, it is known as *essence* or *oil of mirbane*. It is a quite stable compound, unaffected by acids or alkalis, but by acid reducing reagents such as tin and HCl, nitro-benzene is converted into amino-benzene or aniline, $C_6H_5NH_2$, an important intermediate for many dyes. It is a poison.

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O$$

Nitrobenzene cannot be prepared by distilling phenyl chloride or chlorobenzene, C_6H_5Cl, with silver nitrite as we can obtain nitro-methane (p. 90). On further nitration with fuming HNO_3 at about 100°, nitrobenzene forms *m*-dinitrobenzene, $C_6H_4(NO_2)_2$, which is an explosive.

Aniline, amino-benzene or phenylamine, $C_6H_5NH_2$, was first obtained in 1826 by distilling indigo from India, whence the name (Sanskrit *nila*, dark-blue or the indigo plant; the Portuguese called Indian indigo *anil*). It was later discovered in coal-tar and bone-oil. Like methylamine, aniline is a base which may be regarded as derived from ammonia, NH_3, by the replacement of one hydrogen atom by a phenyl group, C_6H_5-. But aniline differs from methylamine in its chemical behaviour as well as mode of preparation. (In the laboratory, aniline is made by the reduction of nitrobenzene with tin and HCl at a temperature not exceeding 90°. It is purified by distillation in steam. Aniline is obtained as aniline hydrochloride, $C_6H_5NH_3Cl$, which is treated with NaOH solution to liberate free aniline.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 3Sn + 6HCl = \underset{\text{Aniline}}{C_6H_5NH_2} + 3SnCl_2 + 2H_2O.$$

Commercially, nitrobenzene is reduced with iron filings, water and a little HCl. Iron filings and water in presence of $FeCl_2$ reduce nitrobenzene to aniline so that the theoretical amount of HCl is not required.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 3Fe + 6HCl = \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O + 3FeCl_2. \quad)$$

Another method, less costly, is to react chlorobenzene with aqueous ammonia under high pressure at about 200°, in presence of cuprous oxide and chloride:

$$\underset{\text{Chlorobenzene}}{2C_6H_5Cl} + 2NH_3 + Cu_2O \xrightarrow{Cu_2Cl_2} \underset{\text{Aniline}}{2C_6H_5NH_2} + Cu_2Cl_2 + H_2O.$$

(Phenol, on heating with zinc chloride and NH_3 to about 300°, yields aniline:

$$\underset{\text{Phenol}}{C_6H_5OH} + NH_3 = \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O.$$)

Properties.—Freshly distilled aniline is a colourless, oily liquid (b.p. 183°) with a characteristic smell which is *not* ammoniacal. On prolonged exposure to light and air, it turns deep brown. It is very sparingly soluble in water and is slightly heavier (sp. gr. 1·022) than it. Benzene, alcohol or ether mixes with aniline readily. It is a very weak base, weaker than ammonia; it forms crystalline salts with acids; aniline hydrochloride, $C_6H_5NH_3Cl$, is obtained by mixing aniline and HCl. The sulphate, $(C_6H_5NH_3)_2SO_4$, is made similarly. These salts are soluble in water; the aqueous solution is strongly acidic due to hydrolysis.

Reactions.—(*i*) With nitrous acid *in the cold,* aniline salts form diazonium salts which give phenol on warming with water. This is called *diazo reaction.* The diazo-salt can be precipitated with alcohol or ether.

$$\underset{\text{Aniline hydrochloride}}{C_6H_5NH_3Cl} + HNO_2 = \underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + 2H_2O.$$

$$C_6H_5N_2Cl + H_2O = \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl.$$

Aliphatic amines, *e.g.*, methylamine, form no diazo-compound but split up into alcohol, nitrogen and water (p. 96). The aromatic diazo compounds are very reactive and may be converted into other types of compounds. Many dyes are derived from diazo compounds.

(*ii*) With alkyl iodide, aniline forms methylamine on heating under a reflux condenser.

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow{CH_3I} \underset{\text{Monomethylaniline}}{C_6H_5NH.CH_3} \xrightarrow{CH_3I} \underset{\text{Dimethylaniline}}{C_6H_5N(CH_3)_2}$$

(*iii*) Aniline readily reacts with acid chlorides or anhydrides forming *anilides* which resemble aliphatic acid amides. These are crystalline and so useful in the identification of amino-compounds.

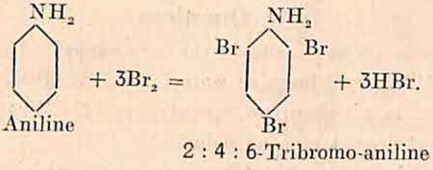
$$\underset{\text{Aniline}}{C_6H_5NH}\overline{\underline{|H + Cl|}}\underset{\text{Acetyl chloride}}{CO.CH_3} = \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + HCl.$$

$$\underset{\text{Aniline}}{2C_6H_5NH_2} + \underset{\text{Acetic anhydride}}{O(OC.CH_3)_2} = \underset{\text{Acetanilide}}{2C_6H_5NH.OC.CH_3} + H_2O.$$

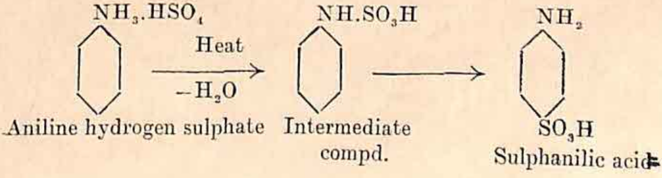
(*iv*) Aniline gives carbylamine reaction with chloroform and alcoholic potash (p. 47), an intolerable smell results from this reaction. Aniline may thus be identified.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH = \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O.$$

(*v*) With chlorine or bromine, aniline reacts quantitatively giving trichloro- or tribromo-aniline. Iodine, however, gives mono-iodo-aniline, $C_6H_4NH_2.I$.



(*vi*) One interesting change that aniline hydrogen sulphate undergoes on heating to about 200° with fuming H_2SO_4, is the formation of sulphanilic acid, used in making certain dyes:



Uses.—Aniline is widely used in many organic syntheses, *e.g.*, for making aniline dyes, indigo, etc., for making certain drugs such as atoxyl or antifebrin.

Acetanilide, antifebrin, $C_6H_5NH.OCCH_3$, is made by boiling under reflux aniline with glacial acetic acid. Acetyl chloride or acetic anhydride may as well be used for glacial acetic acid.

$$\underset{\text{Aniline}}{C_6H_5NH}\boxed{H + HO}\underset{\text{Acetic acid}}{OC.CH_3} = \underset{\text{Acetanilide}}{C_6H_5NH.OC.CH_3} + H_2O.$$

Acetanilide forms white, rhombic plates (m.p. 114°), sparingly soluble in cold, but readily soluble in hot water. It is used in medicine for lowering body temperature and is popularly known as *febri-fuge* or *antifebrin*. It also relieves pain. On hydrolysis with acids, acetanilide gives back aniline and acetic acid:

$$\begin{array}{r|l} C_6H_5NH & OCCH_3 \\ H & OH \end{array} = \underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Acetic acid}}{CH_3COOH}.$$

Questions

1. How is aniline made in the laboratory? How does it react with HCl, HNO_2 and bromine water? I.Sc. 1951, Annamalai Uni

2. How is nitrobenzene manufactured? What are its uses? What product does it give on reduction?

3. What happens when (a) aniline reacts with CH_3I, (b) aniline, chloroform and alcoholic KOH are heated together, (c) aniline is refluxed with glacial acetic acid? Give equations.

4. Write short notes on: diazo reaction, acetylation, and carbylamine reaction.

CHAPTER XX

Phenol, C_6H_5OH, is obtained by replacing a hydrogen atom of the benzene nucleus by a hydroxyl group. This is apparently analogous to aliphatic alcohols, ROH, but unlike the latter, phenol is a weak acid, forming salts with caustic alkalis. The aromatic alcohols, the true analogues of aliphatic alcohols, are benzene derivatives with the $-OH$ group in the side-chain, *e.g.*, benzyl alcohol, $C_6H_5CH_2OH$. This is another important distinction between aliphatic and aromatic compounds. All hydroxy-aromatic compounds, with the $-OH$ group attached to the ring, are called *phenols;* of these, monohydroxy-benzene, C_6H_5OH, the most important member, is simply called phenol (*cf.*, alcohol or ether). Phenol resembles alcohols in many of its reactions and properties for the common $-OH$ group.

The main source of phenol is coal-tar; for this reason as also for its acidic nature, it is popularly known as carbolic acid (*carbo,* coal; *oleum,* oil). The middle oil fraction of coal-tar distillation contains 25-40% of phenols together with some naphthalene (p. 135). On cooling, naphthalene mostly crystallises out and is removed by centrifuging. The liquid is treated with warm NaOH solution, phenols dissolve as sodium phenates. These are treated with H_2SO_4 or CO_2 under pressure to set free phenols. By fractional distillation, carbolic acid is obtained almost pure. About 1·5 lb. of phenol is obtained per ton of coal distilled.

Phenol is manufactured by heating chlorobenzene with sodium carbonate solution under pressure at about 320° in copper vessels, copper acting as a catalyst.

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + Na_2CO_3 + H_2O = \underset{\text{Phenol}}{C_6H_5OH} + NaCl + NaHCO_3.$$

Some phenol is also made by fusing benzenesulphonic acid with caustic soda at about 350°. Sodium phenate formed is extracted with water and decomposed with CO_2 to obtain free phenol. Benzenesulphonic acid is made from H_2SO_4 and benzene (p. 137).

$$\underset{\text{Benzenesulphonic acid}}{C_6H_5SO_3H} + 3NaOH = \underset{\text{Sodium phenate}}{C_6H_5ONa} + Na_2SO_3 + 2H_2O.$$

A recent method involves the hydrolysis of chlorobenzene (made from benzene and HCl in presence of air and catalyst) at about 425°. Pure phenol is thus obtained. The method was discovered in Germany; it is followed in the U.S.A.

There are other methods, theoretically important, for the preparation of phenol, *e.g.*, from aniline by the action of HNO_2 (p. 146), or from salicylic acid by heating with soda-lime (p. 160). Phenol cannot be conveniently obtained from a phenyl halide such as C_6H_5I, with aqueous NaOH (but under drastic conditions, chlorobenzene gives phenol with Na_2CO_3 ; see above).

Properties.—Phenol forms large, colourless prisms (m.p. 42°) soluble in alcohol and ether but only sparingly in water at ordinary temperature. It is rather peculiar that above 68°, it is miscible with water in any proportion. It is volatile in steam. Phenol turns pink on exposure to air. It has a strong, characteristic smell by which it may be recognised. Phenol is a poison ; it is a valuable antiseptic. But it is corrosive. 'Phenyle', the common disinfectant, is a mixture of *cresols*, $C_6H_4(CH_3)OH$, in oil-soap solution.

With NaOH, phenol forms sodium phenate or phenolate, which is soluble in water.

$$\underset{\text{Phenol}}{C_6H_5OH} + NaOH = \underset{\text{Sodium phenate}}{C_6H_5ONa} + H_2O.$$

Sodium phenate and alkyl halides react to give phenol ethers:

$$\underset{\text{Sodium phenate}}{C_6H_5\overline{O|Na + I}|CH_3} = \underset{\text{Phenylmethyl ether}}{C_6H_5{-}O{-}CH_3} + NaI.$$

With acetyl chloride or acetic anhydride, it forms ester:

$$C_6H_5O|\overline{H + Cl}|.OCCH_3 = C_6H_5OOC.CH_3 + HCl.$$

Phenol Acetyl chloride Phenyl acetate

$$C_6H_5OH + (CH_3CO)_2O = C_6H_5O.OC.CH_3 + CH_3COOH.$$

Phenol Acetic anhydride Phenyl acetate Acetic acid

Phenol reacts with PCl_5 to give phenyl chloride:

$$C_6H_5OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl.$$

Phenyl chloride

With H_2SO_4, it readily forms phenolsulphonic acid, and with *dilute* HNO_3, nitrophenol:

$$C_6H_5OH + H_2SO_4 = C_6H_4(OH)SO_3H + H_2O.$$

Phenol Phenolsulphonic acid

$$C_6H_5OH + HNO_3 = C_6H_4(OH)NO_2 + H_2O.$$

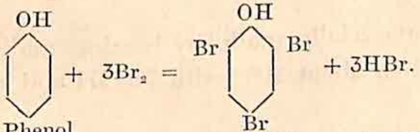
Phenol Nitrophenol

Distilled with zinc dust, phenol is reduced to benzene:

$$C_6H_5OH + Zn = C_6H_6 + ZnO.$$

Phenol Benzene

Phenol and bromine water immediately give a white ppt. of tri-bromophenol, *the reaction is quantitative.*



Phenol 2:4:6-Tribromophenol

Heated with a compound of $ZnCl_2$ and ammonia, phenol forms aniline:

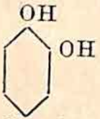
$$C_6H_5OH + NH_3 = C_6H_5NH_2 + H_2O.$$

Phenol Aniline

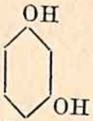
Carbolic acid (as also other phenols) gives the *Liebermann test:* Warm very gently a little phenol with sodium nitrite in H_2SO_4, dilute with water. It turns red, but on adding excess NaOH solution, it becomes blue or green. An aqueous solution of phenol gives a violet coloration with ferric chloride solution.

Uses.—Phenol is mostly used for making synthetic plastics. Bakelite is a phenol-formaldehyde product, named after its discoverer Baekeland of America. Picric acid, an explosive, is trinitrophenol. Phenol is employed in carbolic soaps, powder, etc. for use as antiseptic. Several drugs (*e.g.* aspirin, salicylic acid, etc.) and dyes are made from phenol.

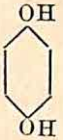
Dihydric phenols, $C_6H_4(OH)_2$, *o*-, *m*-, and *p*-, have the structures:



Catechol



Resorcinol

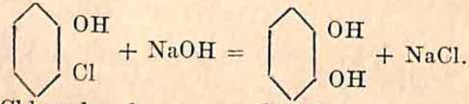


Quinol

They resemble phenol in their general properties but unlike phenol, they are all reducing agents.

Catechol, pyro-catechol, or ortho-dihydroxybenzene, $C_6H_4(OH)_2$, occurs in the Indian *catechu* and was first obtained by the dry distillation of this product, whence the name.

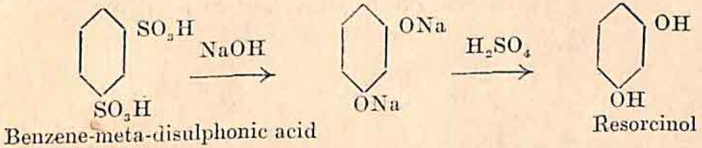
It is commercially made by heating under pressure *o*-chloro-phenol to about 190° with NaOH and a little copper sulphate.



o-Chlorophenol Catechol

Catechol is a colourless, crystalline solid (m.p. 104°), highly soluble in water, alcohol and ether. It sublimes readily and darkens on exposure to air. It gives a green coloration with ferric chloride solution and readily reduces Fehling's solution on warming and ammoniacal silver nitrate in the cold, like an aldehyde. Catechol is used in making adrenalin, a valuable drug, and also as a photographic developer.

Resorcinol, meta-dihydroxybenzene, $C_6H_4(OH)_2$, is technically made by fusing benzene-*m*-disulphonic acid with NaOH at about 270° for about 8 hours. The mass is acidified and resorcinol extracted with ether.

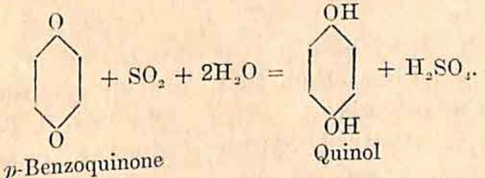


Resorcinol forms colourless needles (m.p. 119°), highly soluble in water, alcohol and ether. It gives a violet coloration with ferric chloride solution. It slowly reduces Fehling's solution and ammoniacal solution of silver nitrate. Resorcinol is used in making certain dyes; it is a remedy for eczema.

Quinol, hydroquinone or *p*-dihydroxybenzene, $C_6H_4(OH)_2$, occurs as a glucoside, *arbutin* which gives quinol on acid hydrolysis, or with *emulsin*. It was first obtained by distilling quinic acid, hence the name *quinol*.

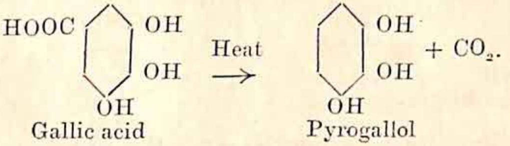
$$\underset{\text{Arbutin}}{C_{12}H_{16}O_7} + H_2O = \underset{\text{Quinol}}{C_6H_4(OH)_2} + \underset{\text{Glucose}}{C_6H_{12}O_6}.$$

It is made by the reduction of *p*-benzoquinone with aqueous sulphur dioxide (hence the name hydroquinone) and extracting the product with ether.



Quinol is a colourless, crystalline solid (m.p. 169°) readily soluble in water. It turns black in air due to oxidation and is a powerful reducing agent; hence its use as a photographic developer. Quinol gives no coloration with ferric chloride solution. It is readily oxidised to quinone, $C_6H_4O_2$.

Pyrogallol, pyrogallic acid or 1:2:3-trihydroxybenzene, $C_6H_3(OH)_3$, occurs in gall nuts as gallic acid, $C_6H_2(OH)_3COOH$, which on heating gives pyrogallol:



Gallic acid Pyrogallol

Commercially, pyrogallol is made by heating gallic acid with half its weight of water in an autoclave. Pyrogallol is a colourless, crystalline solid (m.p. 132°), highly soluble in water but less soluble in alcohol or ether. It gives a red coloration with ferric chloride. An alkaline solution of pyrogallol readily absorbs oxygen and turns dark brown. It is, therefore, used in the estimation of this gas. Pyrogallol is a strong reducing agent; it is a photographic developer. It is used in medicine and also in making certain dyes.

Questions

1. Write a note on the simple physical and chemical properties of either aniline or phenol. I.Sc. 1955, Patna Uni.

2. What is the chemical nature of formalin, carbolic acid, methylated spirit, urea and cane-sugar? Give their simple properties and uses. I.Sc. 1954 Patna Uni.

3. How is phenol isolated from the middle oil fraction of coal tar? How can you obtain from phenol (*i*) salicylaldehyde and (*ii*) a hydroxy-benzoic acid? I.Sc. 1951, E. Punjab Uni.

4. Give the structural formula of fructose, glycerine, urea, lactic acid, acetamide and resorcinol. I.Sc. 1953, Poona Uni.

5. Compare and contrast the properties of ethyl alcohol and phenol.

CHAPTER XXI

Benzyl alcohol, $C_6H_5CH_2OH$, a true aromatic alcohol, occurs free and as ester in jasmine oil, Tolu and Peru balsams, etc.

In the laboratory, it is prepared by reacting benzaldehyde with caustic soda ; a peculiar change takes place in which one mol. of benzaldehyde is oxidised to benzoic acid while another mol. is simultaneously reduced to benzyl alcohol *(Cannizzaro reaction)*:

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + NaOH = \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5COONa.}$$

The commercial method is to boil benzyl chloride with milk of lime (p. 142). Benzyl chloride is made from toluene by chlorination.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{Ca(OH)_2} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

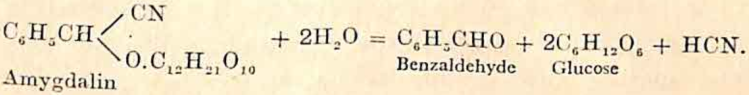
Properties.—Benzyl alcohol is a colourless, pleasant-smelling liquid (b.p. 206°), readily soluble in alcohol or ether but only slightly soluble in water. It is neutral, forms esters with acids, gives benzaldehyde and then benzoic acid on oxidation with chromic acid, benzyl chloride, $C_6H_5.CH_2Cl$, with PCl_5, and benzoxide with Na or K. It is a primary alcohol and resembles methyl or ethyl alcohol.

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow{O} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{O} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

$$C_6H_5CH_2OH + Na \longrightarrow \underset{\text{Sodium benzoxide}}{C_6H_5CH_2ONa}$$

Benzyl alcohol is reduced to toluene by HI. Some ointments contain the alcohol ; the acetate and benzoate are used in perfumery.

Benzaldehyde, oil of bitter almonds, C_6H_5CHO, occurs as a glucoside, *amygdalin*, $C_{20}H_{27}NO_{11}$, in bitter almonds (*amygdale*, almond). This is hydrolysed by boiling mineral acids or by *emulsin* present in the almond but in separate cells. In amygdalin, benzaldehyde cyanhydrin is coupled with two glucose units.



$$\underset{\text{Amygdalin}}{C_6H_5CH\begin{matrix} \diagup CN \\ \diagdown O.C_{12}H_{21}O_{10} \end{matrix}} + 2H_2O = \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Glucose}}{2C_6H_{12}O_6} + HCN.$$

Benzaldehyde is made in the laboratory by boiling benzyl chloride with lead or copper nitrate solution; hydrolysis and then oxidation take place:

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{H_2O} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow{O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

The commercial process is to chlorinate toluene to benzal chloride and hydrolyse it with milk of lime under pressure:

$$\underset{\text{Benzal chloride}}{C_6H_5CHCl_2} + Ca(OH)_2 = \underset{\text{Benzaldehyde}}{C_6H_5CHO} + CaCl_2 + H_2O.$$

By distilling a mixture of calcium benzoate and formate, benzaldehyde may be obtained.

$$(C_6H_5COO)_2Ca + (HCOO)_2Ca = 2C_6H_5CHO + 2CaCO_3.$$

Properties.—Benzaldehyde is a colourless liquid (b.p. 179°), slightly soluble in water but highly soluble in alcohol and ether. It is volatile in steam and has the smell of oil of bitter almonds. Benzaldehyde is used as a flavouring agent and also in making some dyes.

Benzaldehyde resembles acetaldehyde in most of its reactions. Thus on reduction with sodium amalgam, it gives back benzyl alcohol, and on oxidation even by air, forms benzoic acid. With PCl_5, it gives benzylidene or benzal chloride, $C_6H_5CHCl_2$, no HCl being evolved.

$$C_6H_5CHO \xrightarrow{H} C_6H_5CH_2OH \text{ (Benzyl alcohol)}$$

$$C_6H_5CHO \xrightarrow{O} C_6H_5COOH \text{ (Benzoic acid)}$$

$$C_6H_5CHO + PCl_5 = C_6H_5CHCl_2 + POCl_3$$

Benzaldehyde likewise reduces ammoniacal solution of silver nitrate and slowly restores the colour of Schiff's reagent but does not reduce Fehling's solution. It forms cyanhydrin with HCN, phenylhydrazone with phenylhydrazine, oxime with hydroxylamine and so on (pp. 68-69).

But benzaldehyde undergoes Cannizzaro reaction with NaOH, giving benzyl alcohol and benzoic acid (p. 155) unlike acetaldehyde.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + NaOH = \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}.$$

With boiling aqueous-alcoholic KCN, benzaldehyde forms benzoin, a ketonic secondary alcohol:

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO + HOC.C_6H_5} = \underset{\text{Benzoin}}{C_6H_5CH(OH).CO.C_6H_5}.$$

Benzaldehyde does not polymerise or undergo aldol condensation with acids or alkalis nor does it form aldehyde-ammonia ordinarily as does acetaldehyde.

Benzoic acid, C_6H_5COOH, one of the earliest known organic acids, can be easily obtained by heating gum benzoin which contains free benzoic acid and the benzyl ester of benzoic acid, *i.e.*, benzyl benzoate, $C_6H_5COO.CH_2C_6H_5$. Horse's urine contains about 2% of benzoyl glycine, $C_6H_5CO.NH.CH_2COOH$, which, on hydrolysis with HCl, yields benzoic acid and glycine. Scheele thus prepared the acid from urine in 1785.

In the laboratory, benzoic acid may be obtained by oxidising benzyl chloride with alkaline potassium permanganate. Benzyl chloride, soda ash and $KMnO_4$ solution are heated together for about two hours and manganese dioxide formed dissolved in sulphurous acid when benzoic acid separates out. The reaction takes place in two steps:

$$\underset{\text{Benzyl chloride}}{2C_6H_5CH_2Cl} + Na_2CO_3 + H_2O = \underset{\text{Benzyl alcohol}}{2C_6H_5CH_2OH} + 2NaCl + CO_2.$$

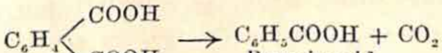
$$\underset{\text{Benzyl alcohol}}{3C_6H_5CH_2OH} + 4KMnO_4 = \underset{\text{Pot. benzoate}}{3C_6H_5COOK} + KOH + 4MnO_2 + 4H_2O.$$

The commercial method is to chlorinate toluene to benzotrichloride, $C_6H_5CCl_3$, and hydrolyse it with milk of lime (p. 143). The free acid is obtained by adding a dilute mineral acid.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5CCl_3} \xrightarrow[Ca(OH)_2]{H_2O} \underset{\text{Calcium benzoate}}{(C_6H_5COO)_2Ca} \xrightarrow{HCl} \underset{\text{Benzoic acid}}{C_6H_5COOH}.$$

Benzoic acid, being sparingly soluble in cold water, separates out and is purified by recrystallisation from boiling water.

By heating phthalic acid (made from naphthalene) with lime, benzoic acid is technically obtained. One —COOH group of phthalic acid is thus removed as CO_2.



$$\underset{\text{Phthalic acid}}{C_6H_4\begin{cases}COOH\\COOH\end{cases}} \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + CO_2$$

Any benzene derivative with a single side-chain will yield benzoic acid on oxidation *e.g.*, toluene, benzyl alcohol, etc. Phenyl cyanide or benzonitrile, C_6H_5CN, gives benzoic acid on hydrolysis:

$$C_6H_5CN + 2H_2O + HCl = C_6H_5COOH + NH_4Cl.$$

Properties.—Benzoic acid forms white, shining plates (m.p. 121°), sparingly soluble in cold, but readily soluble in hot water; it is soluble in alcohol or ether. It sublimes very readily at about 100° and is volatile in steam. The acid vapour, on inhalation, causes sneezing and coughing.

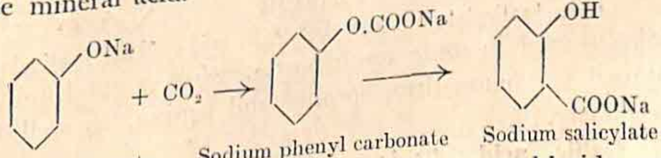
Due to the negative phenyl group, it is about thrice as strong as acetic acid.

Like fatty acids, benzoic acid is monobasic and forms similar derivatives; under suitable conditions, it gives ethyl benzoate, $C_6H_5COO.C_2H_5$, with ethyl alcohol, benzoyl chloride, C_6H_5COCl, with PCl_5, benzoic anhydride, $(C_6H_5CO)_2O$, by reacting its sodium salt with benzoyl chloride; benzoyl chloride and ammonia give benzamide, $C_6H_5CONH_2$, and so on. Distilled with soda-lime, it gives benzene:

$$C_6H_5COOH + 2NaOH = C_6H_6 + Na_2CO_3 + H_2O.$$

Uses.—Benzoic acid and some of its salts such as sodium benzoate are used in medicine as urinary antiseptic. Sodium benzoate is also a food preservative. Aniline blue, a dye, is made from the acid. The acid vapour inhaled disinfects our bronchial tubes.

Salicylic acid, *o*-hydroxy-benzoic acid, $C_6H_4(OH)COOH$, was first obtained in 1838 from *salicin*, a glucoside, whence the name. It occurs as methyl ester *i.e.*, as methyl salicylate, $C_6H_4(OH)COO.CH_3$, in *oil of winter green*, from which it can be obtained by hydrolysis. Salicylic acid is manufactured by heating *dry* sodium phenate to about 130° with CO_2 under pressure in an autoclave for some hours. Sodium phenyl carbonate is first formed, this undergoes a molecular re-arrangement and forms sodium salicylate (*Kolbe Reaction*). Free salicylic acid is liberated with a dilute mineral acid.



Sodium phenate Sodium phenyl carbonate Sodium salicylate

By boiling together phenol, carbon tetrachloride and NaOH, salicylic acid is obtained as the disodium salt:

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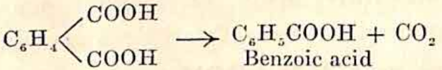

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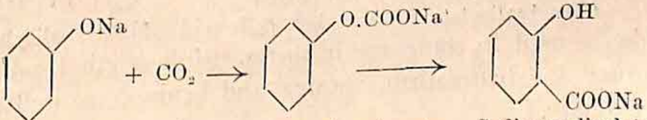
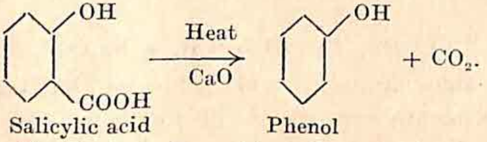


Sodium phenate   Sodium phenyl carbonate   Sodium salicylate

By boiling together phenol, carbon tetrachloride and NaOH, salicylic acid is obtained as the disodium salt:

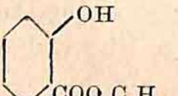
$C_6H_5OH + CCl_4 + 6NaOH = NaO.C_6H_4.COONa + 4NaCl + 4H_2O.$

Properties.—Salicylic acid forms colourless needles (m.p. 156°), sparingly soluble in cold, but readily soluble in hot, water; it is soluble in alcohol or ether. It is both a phenol and an acid and exhibits properties of both. Thus, salicylic acid gives a violet coloration with ferric chloride solution like phenol, and also forms sodium salicylate: $C_6H_4(OH)COONa$, like benzoic acid. Heated with lime, it splits up mainly into phenol and CO_2:

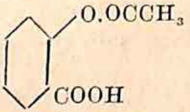


On *slow* distillation, the acid undergoes the same change, but on rapid heating, it sublimes with slight decomposition. With Na_2CO_3, it gives $C_6H_4(OH)COONa$, and with NaOH, the disodium salt, $C_6H_4(ONa)COONa$.

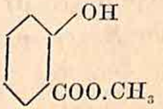
Uses.—Salicylic acid is a good and odourless antiseptic and so used in medicine. Its solution in collodion removes corns from our feet. The acid is largely used as a preservative for food. Phenyl salicylate (*salol*), and acetyl salicylic acid (*aspirin*) are extensively used in medicine. Sodium salicylate is a remedy for rheumatism. Aspirin, acetyl salicylic acid, relieves headache.



Phenyl salicylate



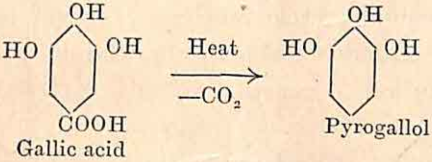
Acetyl salicylic acid



Methyl salicylate

Salol is used in some tooth pastes, while methyl salicylate is used in rheumatism, sprains and bruises, as well as in perfumery.

Gallic acid, 3:4:5-trihydroxybenzoic acid, $C_6H_2(OH)_3COOH$, occurs as a glucoside as well as in the free state in certain plant products such as tannin of gall nuts, tea leaves, etc. It is best obtained by boiling gall nut extract with dilute acids and extracting the gallic acid with ether. It crystallises in needles (m.p. 200°) with one mol. of water. The acid is readily soluble in water, alcohol and ether. It reduces Fehling's solution and absorbs oxygen in alkaline solution like pyrogallol. On heating, gallic acid loses CO_2 and forms pyrogallol.

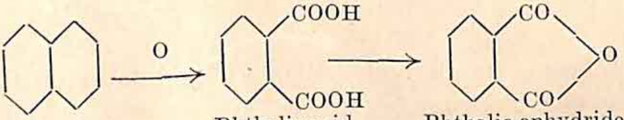


Aqueous solution of gallic acid produces with ferric salts a blue-black precipitate and so used as a marking ink. It is used in making pyrogallol, some inks, drugs and a few dyes.

Ordinary writing inks are mixtures of gallic acid, ferrous sulphate and a little dilute H_2SO_4 and gum. They also contain a little blue dye and phenolic compounds as preservative. Such a mixture writes blue, the H_2SO_4 (which retards rapid oxidation of ferrous sulphate) is neutralised by the alumina in the paper, and ferric gallate is formed (which is blue-black) on exposure to air.

Tannic acid or tannins is the name given to certain astringent, amorphous and practically colourless substances occurring in the bark, wood, leaves, etc. of plants. Many of them being glucosides of gallic acid, are readily broken up on hydrolysis. Tannic acid is soluble in boiling water and alcohol, but almost insoluble in ether. It forms insoluble compounds with gelatine and other proteins, so employed in protecting hides from putrefaction. The process is known as *tanning*. Tanned hide is leather. Tannins are used in dyeing as a mordant, in medicine as an astringent, for treating burns, etc., and also in making writing inks. Indian myrobalan and acacia catechu are important sources of tannic acid.

Phthalic acid, benzene-*o*-dicarboxylic acid, $C_6H_4(COOH)_2$, was once obtained from naphthalene by an accident. A chemist was heating naphthalene, $C_{16}H_8$, with fuming H_2SO_4 and noting the temperature with a thermometer which accidentally broke, the mercury got mixed with the liquid and phthalic acid was obtained in good yield from the fused mass. Mercury acted as a catalyst.

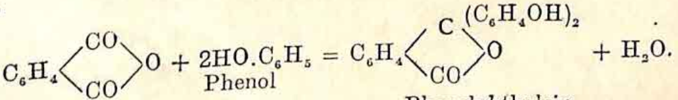


Naphthalene   Phthalic acid   Phthalic anhydride

The oxidation of naphthalene to phthalic acid is now done more easily by passing naphthalene vapour with excess of air over vanadium pentoxide at about 400°. Phthalic acid distils as the anhydride.

Phthalic acid forms colourless prisms (m.p. 213°), readily soluble in water, alcohol and ether. It is largely used in making certain important dyes such as indigo. It is condensed with glycerol into plastics such as *glyptals*. Dimethyl phthalate is an efficient mosquito repellent.

Phenolphthalein is made by heating phthalic anhydride and phenol to about 120° in presence of $ZnCl_2$ or conc. H_2SO_4.



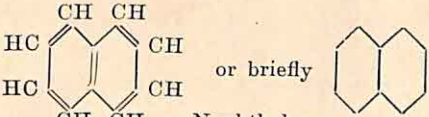
$$C_6H_4\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle O + \underset{\text{Phenol}}{2HO.C_6H_5} = C_6H_4\left\langle \begin{array}{c} C(C_6H_4OH)_2 \\ CO \end{array} \right\rangle O + H_2O.$$

Phthalic anhydride   Phenolphthalein

Phenolphthalein is a white crystalline solid (m.p. 258°) sparingly soluble in water but readily soluble in dilute alkalis (due to phenolic groups) with a deep pink colour. On neutralisation, the colour disappears ; hence its use as an indicator. It is widely used in medicine as a purgative.

Naphthalene, $C_{10}H_8$, as already mentioned, occurs in the middle oil fraction of coal-tar distillation and is exclusively obtained therefrom. About 130 lb. of naphthalene is obtained per ton of coal-tar. On cooling the middle oil, most of it crystallises out and is separated by pressing out the oil. It is purified by sublimation.

Naphthalene forms large, white, shining plates (m.p. 80°) with a characteristic but not unpleasant smell. It is highly volatile at all temperatures, so it always accompanies coal-gas. It is insoluble in water but readily soluble in benzene, ether and hot acohol. It burns with a very luminous flame, depositing much soot. It is volatile in steam. Naphthalene closely resembles benzene in its properties and has the following structure, a fusion of two benzene rings:



Naphthalene

Like benzene, naphthalene is chlorinated to chloronaphthalene, $C_{10}H_7Cl$; nitrated to nitro-naphthalene, $C_{10}H_7NO_2$; and sulphonated to naphthalenesulphonic acid, $C_{10}H_7SO_3H$.

Large quantities of naphthalene are used in making dyestuffs. It is commonly employed as an insecticide and also as a preventive for moths in clothes (*moth balls*).

Questions

1. Give the occurrence and preparation of benzaldehyde. Compare and contrast its properties with those of acetaldehyde. What are its important uses? I.Sc. 1952, E. Punjab Uni.

2. How is salicylic acid prepared? Give its most important properties and uses. Give one example with formula of each of the two types of esters it forms. I.Sc. 1952, E. Punjab Uni.

3. Give *one* method of preparation, *two* properties and *one* use of any *three* of the following: (*a*) chloroform, (*b*) ethyl iodide, (*c*) aniline, (*d*) salicylic acid and (*e*) phenol. I.Sc. 1953, Patna Uni.

4. Describe *one* method of preparation and *two* chemical properties of any *three* of the following: (*i*) benzoic acid, (*ii*) cyanogen, (*iii*) ethylamine, and (*iv*) nitrobenzene. I.Sc. 1954, Poona Uni.

5. What is the structural formula for naphthalene? How is it obtained? Mention its chief properties and uses.

CHAPTER XXII

Our food.—The human body may be roughly compared with an engine which derives its energy for doing work from the fuel supplied in the form of oil or coal. Food which serves as the fuel for our body, consists almost wholly of organic compounds; the energy stored therein is slowly liberated on oxidation in our system. Thus when one pound of cane-sugar is 'burnt' in our body in presence of oxygen of the air we inhale to CO_2 and H_2O, it gives 1350 kilo calories of heat, which is sufficient to raise about 4½ gallons of water from the room temperature to the boiling point. Unlike plants, we cannot build up organic compounds from inorganic sources such as air, water and mineral matters. Our food comes from plants and animals; it supplies heat (with which we maintain a constant body temperature) and energy for the work we do; it also helps building up new tissues and repairing decayed ones. Our food may be broadly divided into three groups, *viz.*, carbohydrates, fats, and proteins. Besides these, mineral salts and vitamins are also essential for our existence. By *balanced diet* is meant a proper selection of various kinds of food in right quantities so as to ensure sufficient calories, and adequate supply of all these items. An adult should daily take 4 oz. of protein, 3 oz. of fat and 15 oz. of carbohydrate (calculated on dry basis) in addition to sufficient water, salts, and oxygen. The food requirements of old people, adults and children are, of course, different. Growing children, for example, require more proteins than adults. Then again, the energy and food requirements of different kinds of workers are also somewhat different. Thus, a wood-cutter requires, on an average, about 5000 kg. calories per day but a tailor requires only about 2500 kg. calories and a sedentary woman's daily need is 2100 kg.

calories. The food habits of different peoples are different ; a good food must conform to our national habits. What is eatable to one set of people, may be uneatable to another ; *e.g.*, Muslims take beef but not Hindus ; certain sects in India do not touch fish or meat.

We shall now discuss the various constituents of our diet:

Carbohydrates.—Rice, maize, wheat, potato, cane-sugar, barley, sago etc. belong to this group. They are the cheapest source of energy. Starch alone constitutes practically the whole diet of poor men in India ; it is partly converted into fat in the system. Starch also contain some protein (*e.g.* gluten). One lb. of carbohydrate gives 1800 kilogram calories of heat. We can digest raw starch but cooked starch is more readily digested. Starch is hydrolysed to glucose by enzymes through a series of changes, glucose then goes to the blood and gets oxidised finally to CO_2 and water. Diabetic patients cannot break up starch or sugar beyond the glucose stage. Insulin, secreted by the pancreas into the blood, helps the oxidation of glucose. In diabetes, this secretion is seriously hampered. Ripe fruits contain sugars, root-vegetables (tubers) are rich in carbohydrates (starch, sugars). Lactose (or milk-sugar) is a disaccharide like cane-sugar. Honey, nectar of flowers, etc. consist of sugars.

The starchy foods are not, however, pure carbohydrates : thus rice is 75-80% starch, it also contains some fat and protein. Wheat has 65-70% starch and about 14% protein. All these products invariably contain some mineral matter. Glycogen or animal starch, $(C_6H_{10}O_5)n$, is a reserve food in our liver which converts it into glucose readily in times of need. We cannot digest the cellulose present in our vegetable diet. It, however, plays an important role, *viz.*, helping the passage of food along the intestine. Ptyalin of our saliva, an enzyme, hydrolyses starch into simpler sugars like maltose in slightly alkaline solution. Further hydrolysis upto glucose is effected in the intestine by the pancreatic *amylase*.

Fats.—These (also called *lipids*) give more calories than carbohydrates or proteins, weight for weight; one part of fat is equivalent to 2·25 parts of carbohydrates as regards calories. These are stored in the tissues as reserve food; during fast or starvation, fats supply the calories necessary for our existence. Butter, ghee, oils such as mustard, cocoanut, sesame oils, etc. fish-oils or *vanaspati* are the common fats we take. Besides these, small amounts of fats are present in wheat, rice, etc. Carbohydrates, as already mentioned, are partly transformed into fat in our system. Only a few fats serve as food; some *e.g.*, castor oil or croton oil are strong purgatives. Boiled fats are, however, less readily digested than the raw. Oils are more easily digested than fats. Fats are split up during digestion; the typical human fat is built from the remnants.

Proteins.—These are essential constituents of all living cells; no plant or animal can live without proteins. We can do without carbohydrates or fats for a considerable period; these may be formed in our system from the proteins. Plants can build up proteins from inorganic sources but not animals. We require both animal and vegetable proteins; in fact, we require some eight amino-acids (called essential amino-acids) which must be present in our food. Foods, rich in protein, are fish, meat, oat-meal, peas, cheese, egg, wheat, nuts, etc. Potato contains about 2%, banana about 1·5%, cow's milk about 3%, bread about 6·5%, butter about 0·75% of proteins. We cannot digest any protein ; all the proteins of our food are not digested to the same extent.

Proteins supply about the same calories per lb. as carbohydrates, but the latter are much cheaper. The Indian diet, in general, is rather poor in protein mainly due to the cost. 1 g. protein per kg. body weight per day is our minimum protein requirement.

Mineral matters.—We take common salt daily, which supplies the HCl to our stomach. Our bones contain calcium phosphate, and teeth calcium fluoride ; hæmoglobin of our blood has iron. The average human body consists of 1·5% Ca, 1% P, 0·35% K, 0·25% S, 0·15% Na, and 0·15% Cl, besides 65% O, 18% C, 10% H and 3% N. Traces of iodine are also present. Most of these inorganic constituents occur in our food. The growing child requires more calcium for bone formation ; calcium carbonate (chalk powder) is mixed in wheatflour in the U. K. to make up the calcium deficiency.

Vitamins.—Our health and growth very largely depend on vitamins which occur in *fresh* foods. We require these only in minute quantities. Their deficiency causes various diseases and disorders in our system. These are known as vitamin A, B, C, D, E and K. Some have been synthesised.

Vitamin A (fat-soluble) promotes growth. It occurs in many fats *e.g.* cod-liver oil, butter, egg yolk fat, etc. but not in lard or olive oil. Fish liver is a rich source of this vitamin. Carrot, green vegetables and tomato contain this. Its deficiency diminishes our capacity to resist bacterial infection and also causes night blindness. It is fairly resistant to heat. Only animals synthesise it, often from *β*-carotene.

Vitamin B (water-soluble) occurs widely in our foods, *e.g.*, in vegetables, rice, wheat, etc. as well as in yeast. It also promotes growth ; its deficiency causes beri-beri. It consists of several constituents such B_1, B_2, B_6 and is commonly known as B-complex.

Vitamin C or ascorbic acid (water-soluble) occurs in fresh fruits and vegetables (particularly in lemon, orange, tomato, etc.) It is largely destroyed on storing and cooking. Its deficiency leads to scurvey, a skin disease.

Vitamin D (fat-soluble) promotes growth and prevents rickets which is due to non-deposition of calcium phosphate in bones of children. It acts in presence of Vitamin A. It occurs in fats (particularly in fish-liver oils), butter, yeast, etc. *Calceferol,* obtained from ergosterol by ultra-violet exposure, is Vitamin D_4 ; Vitamin D_3 is formed in our body when we are in direct sunlight.

Vitamin E is present in milk, wheat germ, leaves of plants, etc. ; its deficiency causes sterility. It is stable to heat but readily oxidised. Lettuce and alfalfa are rich sources of this vitamin.

Vitamin K occurs in green plants, particularly in alfalfa. Hog liver and hempseed also contain this vitamin. It stops hæmorrhage and causes clotting of blood.

APPENDIX—A

IDENTIFICATION OF SOME ORGANIC COMPOUNDS

1. **Methyl alcohol, CH_3OH,** is a colourless, neutral, inflammable liquid (b.p. 64°), miscible with water. It liberates hydrogen with metallic sodium. Distilled with pot. dichromate and dilute H_2SO_4, it gives formic acid. Pure methanol does not give iodoform with iodine and Na_2CO_3 solution.

2. **Ethyl alcohol, C_2H_5OH,** is a colourless, neutral, inflammable, liquid (b.p. 78·5°), miscible with water. It gives hydrogen with metallic sodium. Warmed with iodine and Na_2CO_3 solution, it forms yellow crystals of iodoform. Heated with pot. dichromate and dilute H_2SO_4, acetaldehyde (but not acetic acid) results from ethyl alcohol. On heating alcohol with sodium acetate and conc. H_2SO_4, ethyl acetate with a fruity odour is formed.

3. **Glycerol, $CH_2OH.CHOH.CH_2OH$,** is a colourless, odourless, viscous liquid (b.p. 290°) with a sweet taste. It is miscible with water, insoluble in chloroform or ether, and neutral to litmus. Heated with powdered potassium hydrogen sulphate, it gives acrolein which has a pungent and irritating odour. The pink colour produced on adding phenolphthalein to dilute borax solution disappears on adding glycerol; the colour reappears on warming.

4. **Chloroform, $CHCl_3$,** is a colourless, heavy, neutral liquid (b.p. 61°) with a sweet smell. It is soluble in alcohol and ether but practically insoluble in water. Its vapour turns the edge of the Bunsen flame green. On gently warming chloroform, aniline and alcoholic KOH, the foul and disgusting odour of phenyl isocyanide is produced (*carbylamine reaction*). It reduces Fehling's solution on warming

and gives a red coloration on gently warming with a little resorcinol and strong NaOH solution.

5. **Iodoform, CHI_3,** is a yellow, crystalline solid (m.p. 119°) with a characteristic odour. It is insoluble in water but readily soluble in alcohol or ether. On heating in a dry test-tube, iodoform gives off violet vapour of iodine. It also gives the carbylamine reaction like chloroform.

6. **Acetone, CH_3COCH_3,** is a colourless, volatile liquid (b.p. 56°) with a pleasant smell. It is miscible with water, alcohol or ether. It gives the iodoform test like ethyl alcohol but unlike the latter, it forms iodoform with I in KI and ammonia (instead of NaOH or Na_2CO_3). It gives a violet-red colour with a freshly prepared solution of sodium nitro-prusside and dilute NaOH solution. On shaking with a conc. solution of sodium bisulphite, acetone gives a white ppt.

7. **Formaldehyde, HCHO,** is a gas with a pungent odour. The aqueous solution readily reduces Fehling's solution, ammoniacal solution of $AgNO_3$, and also restores the colour of Schiff's reagent. It gives a purple-red colour on heating with a dilute solution of phenylhydrazine hydrochloride and a fresh solution of sodium nitro-prusside, followed by addition of pot. ferricyanide solution and conc. HCl.

8. **Phenol, carbolic acid, C_6H_5OH,** is a colourless, crystalline solid (m.p. 42°) which turns pink in air. It has a strong, characteristic smell, is soluble in alcohol and ether but slightly soluble in water at ordinary temperature. Phenol gives a deep violet colour with *neutral* ferric chloride solution; with bromine water, it forms a white ppt. of tribromophenol even in dilute aqueous solution. Phenol is best detected by *Liebermann's test* (p. 151). It readily

dissolves in NaOH solution as sodium phenate but not in Na_2CO_3 solution.

9. **Urea, carbamide, $H_2N.CO.NH_2$,** is a colourless, odourless, crystalline solid (m.p. 132°), readily soluble in water or alcohol but insoluble in ether. The aqueous solution is neutral to litmus. With conc. HNO_3 it forms a ppt. of urea nitrate, insoluble in HNO_3; with oxalic acid, it gives a white ppt. of urea oxalate. Urea gives the biuret test (p. 108). By nitrous acid ($NaNO_2$+dil. H_2SO_4) it is decomposed, and N_2 and CO_2 evolve.

10. **Aniline, $C_6H_5NH_2$,** is a colourless oily liquid (b.p. 183°) with a peculiar smell; it is sparingly soluble in water but readily soluble in benzene, alcohol or ether. It gives carbylamine reaction with chloroform and alcoholic KOH. It forms crystalline salts with acids, which are soluble in water. Shaken with bleaching powder solution, it gives a transient purple colour which turns brown on standing. Aniline forms a diazo salt with HNO_2 (p. 146), which gives a scarlet dye with β-naphthol in NaOH solution.

11. **Formic acid, HCOOH,** is a colourless liquid (b.p. 100·5°), miscible with water, alcohol or ether. It has a pungent odour and produces painful blisters on the skin. With cold, conc. H_2SO_4, it gives CO which burns with a lambent blue flame. A neutral formate gives with neutral $FeCl_3$ a deep red colour which forms a brown ppt. of basic ferric salt on boiling. Unlike acetic acid, it reduces ammoniacal solution of $AgNO_3$ on boiling, and reduces mercuric chloride to mercurous chloride (white ppt.) on warming. Formic acid also decolorises acid or alkaline $KMnO_4$ solution in the cold. It turns litmus red and gives CO_2 with Na_2CO_3.

12. **Acetic acid, CH_3COOH,** is a colourless liquid (b.p. 118°), readily soluble in water, alcohol and ether. It turns litmus red and gives CO_2 with Na_2CO_3. A neutral acetate gives with neutral ferric chloride solution a deep red colour which forms a brown ppt. of basic acetate on boiling. The acid, however, does not reduce ammon. $AgNO_3$, $HgCl_2$ or $KMnO_4$ (*cf.* formic acid). Heated with conc. H_2SO_4 and ethyl alcohol, it gives the fruity, pleasant odour of ethyl acetate. Heated in a dry test-tube, a dry acetate and arsenious oxide give off a very repulsive odour of cacodyl oxide (a poison).

13. **Oxalic acid, HOOC.COOH,** forms colourless, crystals with 2 mols. of water. On heating, the acid dissolves in its water of crystallisation. It is soluble in water and alcohol. Heated with conc. H_2SO_4, it splits into CO_2 and CO, the former turns lime-water milky. Acid $KMnO_4$ at 60° decomposes oxalic acid to CO_2 and gets decolorised, but alkaline $KMnO_4$ remains unaffected by the acid. With $CaCl_2$ solution, a neutral solution of an oxalate gives a white ppt. of calcium oxalate, insoluble in acetic acid but soluble in dilute HCl.

14. **Citric acid, $HOOC.CH_2.C(OH)COOH.CH_2.COOH$,** is a colourless, crystalline solid (m.p. 100°), readily soluble in water and alcohol. Heated with conc. H_2SO_4, CO_2 and CO are evolved, the former turns lime-water turbid ; it does not char. With $CaCl_2$ solution, a neutral citrate gives no ppt. in the cold, but *on boiling,* a white ppt. of calcium citrate appears, insoluble in acetic acid. A citrate and $CaCl_2$ solution, however, give a ppt. of calcium citrate in the cold on adding NaOH solution.

15. **Benzoic acid, C_6H_5COOH,** is a colourless, crystalline solid (m.p. 121°) with a faint aromatic odour. It sublimes readily, is soluble in alcohol, ether, and hot water ; from

hot aqueous solution, it comes out in glistening plates on cooling. With ferric chloride, neutral benzoates give a buff coloured ppt. of basic ferric benzoate, soluble in NH_4OH. Heated with soda-lime, it gives benzene.

16. **Salicylic acid, $C_6H_4(OH)COOH$** (1 : 2), is a white, odourless, crystalline compound (m.p. 156°), readily soluble in alcohol and ether but very slightly soluble in water. Aqueous-alcoholic solution of the acid gives an intense purple colour with ferric chloride. It yields phenol (recognised by its smell) on heating with soda-lime. Heated with conc. H_2SO_4 and methyl alcohol, it gives methyl salicylate or oil of wintergreen, having a characteristic smell. The acid dissolves in Na_2CO_3 solution.

17. **Tartaric acid, HOOC.CHOH.CHOH.COOH,** is a colourless, crystalline solid, readily soluble in water, less so in alcohol. The acid and its salts char on heating, giving off a smell of burnt sugar. On warming with conc. H_2SO_4, it chars with the liberation of CO_2, CO, etc. A neutral tartrate reduces ammoniacal solution of silver nitrate on warming to a mirror of silver. A neutral tartrate in aqueous solution gives with $CaCl_2$ solution a white ppt. of calcium tartrate in the cold, soluble in acetic acid (*cf.*, citric acid) or conc. NaOH solution. On adding fresh $FeSO_4$ solution, H_2O_2 and then NaOH solution in excess to a solution of tartaric acid or a tartrate, an intense violet colour is produced.

18. **Benzene, C_6H_6,** is a colourless liquid (b.p. 80·4°) with a peculiar odour, insoluble in water but readily soluble in alcohol, acetone, ether, etc. It is lighter than water and burns with a smoky flame. With conc. H_2SO_4 and HNO_3, it forms nitrobenzene on warming on a water-bath ; the latter, an oily yellow liquid, has the odour of crushed bitter almond.

19. **Nitrobenzene, $C_6H_5NO_2$,** is a pale yellow, heavy liquid (b.p. 209°) with an odour of bitter almond. It is almost insoluble in water but readily soluble in ether, alcohol, etc. On warming with fuming HNO_3 and H_2SO_4, it gives solid *m*-dinitrobenzene (m.p. 90°). On reduction with zinc and dilute H_2SO_4, nitrobenzene yields aniline which may be identified by the diazo-reaction (see aniline).

20. **Benzaldehyde, C_6H_5CHO,** is a colourless, oily liquid (b.p. 179°) with the smell of bitter almonds. It is insoluble in water but highly soluble in alcohol and ether. With a saturated solution of $NaHSO_3$, it gives, on shaking, a white, crystalline compound. Benzaldehyde reduces ammon. solution of $AgNO_3$ but not Fehling's solution. With 30% NaOH and warming, it gives benzyl alcohol and sodium benzoate by *Cannizzaro reaction.* On adding conc. HCl in excess, benzoic acid separates. Alkaline $KMnO_4$ oxidises benzaldehyde to benzoic acid.

21. **Phthalic acid, $C_6H_4(COOH)_2$,** is a colourless, crystalline solid (m.p. 213°), soluble in hot water, alcohol, and ether. It dissolves in Na_2CO_3 solution with evolution of CO_2. Heated with soda-lime, it yields benzene. Fused in a dry test-tube with phenol and conc. H_2SO_4, it forms phenolphthalein which gives a bright red colour with NaOH solution. Fused with resorcinol and conc. H_2SO_4 likewise, it yields fluorescein which gives, in NaOH solution, an intense green fluorescence.

APPENDIX—B

NUMERICAL EXERCISES IN ORGANIC CHEMISTY

1. 0·1376 g. of cane-sugar was burnt completely in a combustion tube. Find the increase in weight of the calcium chloride tube and of the potash bulbs. (*Ans.* 0·0797 g and 0·2124 g.).

2. An organic compound has 41·62% C, 4·05% H, 8·10% N. 0·2422 g. of it gave 0·3268 g. of barium sulphate in a sulphur determination. Find its empirical formula. (*Ans.* $C_6H_7O_3NS$).

3. 20 vols. of a hydrocarbon, mixed with 80 vols. of oxygen, gave 60 vols. after explosion and 20 vols. after shaking with KOH solution. What is the gas? (*Ans.* C_2H_4). I.Sc. 1950, Calcutta Uni.

4. 20 c.c. of a gaseous hydrocarbon were exploded with 66 c.c. of oxygen. Residual gases after cooling occupied 56 c.c. On treatment with KOH the volume decreased to 16 c.c. The remaining gas was oxygen only. What is the gas? (*Ans.* C_2H_2). I.Sc., 1953 Rajputana Uni.

5. An organic compound on analysis gave 92·3% C and 7·68% H. It reacted vigorously with Cl_2 and ozone, and also decolorised dilute $KMnO_4$ solution in the cold. Its vapour density was 13. What are the empirical and molecular formulae of the compound? (*Ans.* C_1H_1; C_2H_2). Higher Sec. Exam. 1948, Delhi.

6. A compound A, on analysis, was found to contain 52·2% C and 13·04% H. Its vapour density was 23. On oxidation with $K_2Cr_2O_7$ and H_2SO_4, it gave acetaldehyde and with I_2 and NaOH gave iodoform on warming. The b.p. of A was 78°. What are the empirical, molecular and structural formulæ of A? (*Ans.* $C_2H_6O_1$, C_2H_6O, $CH_3.CH_2.OH$). Higher Sec. Exam. 1949, Delhi.

7. 1·195 g. of a compound, on analysis, gave carbon 0·12 g., hydrogen 0·01 g. and chlorine 1·065 g. Its vapour density was found to be 59·75. Establish the molecular formula. (*Ans.* $CHCl_3$). Higher Sec. Exam. 1952, Delhi.

8. A compound contains 40·67% C and 8·47% H; 0·1475 g. of it gave, on combustion, 28·0 c.c. of nitrogen at N.T.P. Its mol. wt. is 59. What is its molecular formula? (*Ans.* C_2H_5ON).

9. A compound X contains C, H and Cl. In chlorine estimation, 0·1791 g. of it gave 0·2285 g. of AgCl. Calculate the p.c. of Cl, and the mol. wt. of X assuming that X has only one atom of chlorine per mol. (*Ans.* 31·55% ; 112·5).

10. Calculate the empirical formula of a dibasic acid, 0·1328 g. of which, on combustion, gave 0·2816 g. of CO_2 and 0·0432 g. of water. What is its molecular formula if 0·3040 g. of its silver salt gave 0·1728 g. of silver on ignition? (*Ans.* $C_4H_3O_2$; $C_8H_6O_4$).

11. 0·1395 g. of a monoacid base gave, on combustion, 0·396 g. of CO_2 and 0·0945 g. of water; 0·2325 g. of it yielded 28 c.c. of N_2 at N.T.P. 0·596 g. of its platinichloride, on ignition, gave 0·195 g. of Pt. Find the mol. formula of the base. (*Ans.* C_6H_7N).

12. Tartaric acid has 32·0% C, 4·0% H, the rest is oxygen. Its silver salt has 59·34% Ag. Its methyl ester has a vapour density of 89. What is the basicity of the acid? (*Ans.* 2).

13. Citric acid contains 37·50% C, 4·17% H, the balance being oxygen. Its silver salt has 63·16% Ag. Its ethyl ester has a mol. wt. of 276. What is its basicity? (*Ans.* 3).

14. A monobasic acid has 62·07% C, 10·34% H, the rest being oxygen. 0·5511 g. of its anhydrous barium salt gives 0·3501 g. of $BaSO_4$. Find its molecular formula; Ba = 137·4. (*Ans.* $C_6H_{12}O_2$).

15. A volatile organic liquid weighing 0·1185 g. occupied, on vaporisation, 24 c.c. at 12°C and 760·5 mm pressure. Calculate its mol. wt. (*Ans.* 146·1). I.Sc. 1943, Andhra Uni.

16. 20 c.c. of a solution containing 6·24 g. of an acid per litre, required for neutralisation 22 c.c. of alkali containing 3·6 g. of NaOH per litre. Calculate the equivalent weight of the acid. If its basicity is 2, what is its mol. wt.? (*Ans.* mol. wt. = 126·06). I.Sc. 1944, Madras Uni.

17. If 100 c.c. of ethane, C_2H_6, be exploded with an excess of oxygen, what will be the contraction in volume? If the gas mixture, after explosion, is shaken with NaOH solution, what further contraction will take place? Assume all vols. to be measured at constant laboratory temperature and pressure. (*Ans.* 250 c.c., 200 c.c.). I.Sc. 1945, Madras Uni.

18. A compound has 64·68% C, 13·51% H, and 21·62% O. Its vapour density is 37. It is decomposed only by strong HI to an alkyl iodide having 81·41% I. What is the structure of the compound? (*Ans.* C_2H_5-O-C_2H_5).

19. 0·109 g. of a monobromo-paraffin gave on analysis 0·088 g. CO_2 and 0·045 g. water; 0·185 g. of it gave 0·319 g. AgBr. Find the molecular formula of the compound. (*Ans.* C_2H_5Br). I.Sc. 1931, Bombay Uni.

20. What volume of oxygen is required for the complete combustion of 100 c.c. of ethylene? (*Ans.* 300 c.c.). I.Sc. 1943, Punjab Uni.

21. A substance consisting of carbon, hydrogen and nitrogen only, gave 65·45% C, 9·1% H and 25·45% N on analysis. On hydrolysis, it liberated as ammonia its nitrogen and formed a substance having 48·6% C and 8·1% H. What are the two substances? (*Ans.* CH_3CN, CH_3COOH).

22. A substance has 61·01% C, 15·25% H, and 23·73% N. With HNO_2, it yields an alcohol and N_2. The alcohol has 60·00% C, and 13·33% H; which, on careful oxidation, yields another substance of vapour density 29. The last compound forms an oxime and a bisulphite derivative with $NaHSO_3$, but does not reduce Fehling's solution. What was the original substance? (*Ans.* $C_3H_7NH_2$; the alcohol is $CH_3.CHOH.CH_3$).

23. An organic liquid contains 32·0% C, 6·67% H and 18·7% N; its vapour density is 38. What structural formulae can it have? (*Ans.* $CH_3.CH_2.NO_2$ or $CH_3.CH_2.O.NO$).

24. In the determination of N_2 by Kjeldahl's method, an organic compound weighing 0·100 g. gave enough NH_3 to neutralise 28·5 c.c. of 0·1N HCl. What is the percentage of N_2 in the compound? (*Ans.* 39·9%).

25. What weight of oxygen is necessary to burn completely 1·5 g. of ethane? (*Ans.* 5·595 g).

26. 2·00 g. of a monohydric alcohol, when treated with metallic sodium, set free 372 c.c. of H_2 at N.T.P. What is the mol. wt. of the alcohol? (*Ans.* 60).

27. Calculate the volume of N_2 at 18° and 740 mm that will evolve from 1·4 g. of amylamine hydrochloride, $C_5H_{11}NH_3Cl$. (*Ans.* 138·8 c.c.).

28. 0·4576 g. of a compound, on boiling with excess of KOH solution, gave NH_3 which neutralised 37·8 c.c. of N/10 H_2SO_4. The resulting alkaline solution, on acidification, gave a crystalline ppt., 0·0976 g. of which gave 0·2464 g. of CO_2 and 0·432 g. of water. What was the original compound? (*Ans.* $C_6H_5.CO.NH_2$).

29. A substance gave on analysis 66·45% C, 9·1% H and 25·45% N. It gave NH_3 on hydrolysis, and another compound having 48·6% C, and 8·1% H. Calcutta the formulæ of the original and the resulting compound. (*Ans.* C_2H_5CN; C_2H_5COOH).

30. 0·277 g. of an ester was boiled with 50 c.c. of N/10 NaOH until reaction was complete, the resulting liquid required 18·5 c.c. of N/10 HCl for neutralisation. What is the mol. wt. of the ester assuming that it resulted from a monohydric alcohol and a monobasic acid? (*Ans.* 88).

31. 0·6 g. of a simple triglyceride required 16·5 c.c. N/2 KOH for complete hydrolysis. What is the mol. wt. of the triglyceride? The silver salt, obtained from the pot. salt of the monobasic acid by hydrolysis, gave 64·6% Ag. Calculate the mol. wt. of the acid. (*Ans.* 218; 60·2).

32. A crystalline solid contains 27·3% C, 4·55% H, and 31·8% N. Boiling aqueous NaOH slowly liberates NH_3 from the compound; the solution, on evaporation to dryness and being heated with conc. H_2SO_4, gives CO and CO_2. Heated with ethyl alcohol and H_2SO_4, the original compound gave an ester (vapour density 73) and ammonium sulphate. Deduce the mol. formula of the starting solid. (*Ans.* $(CO.NH_2)_2$).

33. A compound has 64·8% C, 13·6% H; the rest is O. What is its empirical formula? Taking it as the molecular formula, write down the possible structural formulæ. (*Ans.* $C_4H_{10}O$; $C_2H_5.O.C_2H_5$, $CH_3.O.C_3H_7$, C_4H_9OH, etc.).

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